APPLICATIONS AND FUTURE PERSPECTIVES OF PHOTOCATALYTIC COATINGS FOR AIR PURIFICATION AND SELF CLEANING

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"APPLICATIONS AND FUTURE PERSPECTIVES OF PHOTOCATALYTIC COATINGS FOR AIR PURIFICATION AND SELF CLEANING"** was prepared by **LEE TONG XIN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

The availability of safe and clean air is one of the most pressing worldwide challenges today. Air pollution will cause severe toxicological repercussions for human health and the ecology. As a result, an effective air purification and self-cleaning technology are required to address the air pollution dilemma. Photocatalytic coating has been the subject of numerous investigations since it appears to be a potential solution for air treatment in the next decades. This study presented a comprehensive and detailed review of recently published publications on the use of photocatalytic coating in the treatment of air. From the review findings on current photocatalytic coating achievements and technologies, air contaminants' removal effectiveness is mostly by using titanium dioxide. Modified titanium dioxide by doping containing metal or non-metal can also enhance the photocatalytic coating efficiency by reducing the conduction band or increasing the valance band; thereby, the bandgap is minimised. For most of the pollutants found in the air, the removal effectiveness was greater than 80%. Furthermore, this study described recent photocatalytic coating developments in air purification and self-cleaning as well as photocatalytic coating's potential in the future development to address the challenges of environmental requirements. This study also revealed the shortcomings and limitations of recently published articles, along with recommendations for uncovering areas that have yet to be studied. Due to the fact that most of the publications were conducted on a bench-scale without attempting to scale up the treatment process to a larger extent, this research underlined the urgent need to adopt titanium dioxide nanoparticles at an industrial scale to meet the environmental criteria. Furthermore, more research into visible light design was encouraged.

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LIST OF SYMBOLS / ABBREVIATIONS

γ_{sv}	interfacial tensions at solid-vapour phase
γ_{sl}	interfacial tensions at solid-liquid phase
γ_{lv}	interfacial tensions at liquid-vapour phase
θ	solid surface's intrinsic contact angle
θ_w	theoretical value of Wenzel's contact angle
r	ratio of the actual solid-liquid contact area to predicted area
e^-	electron
h^+	hole
$^{\bullet}OH$	hydroxyl radicals
$^{\bullet}O_2^-$	superoxide radical anions
hv	energies
a_o	lattice constants
b_o	lattice constants
c_o	lattice constants

Ag	Silver
Au	Gold
Bi_2O_3	Bismuth (III) oxide
C	Carbon
Ce	Cerium
$CHCl_3$	Chloroform
Cl	Chlorine
CO	Carbon monoxide
CO_2	Carbon dioxide
Cr	Chromium
Cu	Copper
F^-	Fluoride
Fe	Iron
Fe_2O_3	Iron (III) oxide
GO	Graphene oxide
HNO_3	Nitric acid
H_2O	Water

$InVO_4$	Indium vanadate
La	Lanthanum
MnO	Manganese (II) oxide
NaCl	Sodium chloride
N	Nitrogen
N_2	Nitrogen gas
Nd	Neodymium
NH_3	Ammonia
Ni	Nickel
NO	Nitric oxide
NO_3^-	Nitrates
N_2O	Nitrous oxide
NOx	Nitrogen oxide
NO_2	Nitrogen dioxide
O_2	Oxygen
O_3	Ozone
Pb	Lead
Pd	Palladium
PM	Particulate matter
Pt	Platinum
Rh	Rhodium
Ru	Ruthenium
SiO_2	Silicon dioxide
SnO_2	Tin (IV) oxide
SO_2	Sulphur dioxide
SOx	Sulphur oxide
Ti	Titanium
TiO_2	Titanium dioxide
V	Vanadium
V_2O_5	Vanadium pentoxide
WO_3	Tungsten trioxide
ZnO	Zinc oxide

ACF	Activated carbon filters
API	Air Pollutant Index
BTEX	Benzene, toluene, ethylbenzene and *o*-xylene
CA	Contact angle
CB	Conduction band
COVID-19	Coronavirus disease
DOE	United States Department of Energy
ES	Electrostatic filters
ESP	Electrostatic precipitator
E_g	Energy bandgap
EY	Eosin yellowish
GAC	Granular activated carbon
GDP	Gross domestic product
GI	Gastrointestinal
HEPA	High efficiency particulate air filters
IT	Intermediate target
LED	Light-emitting diode
LSPR	Localised surface plasmonic resonance
MB	Methylene blue
MO	Methyl orange
MPPS	Most penetrating particle size
NACE	National Association of Corrosion Engineers
NP	Nanoparticles
PAC	Powdered activated carbon
PAHs	Polycyclic aromatic hydrocarbons
PDMS	Polydimethylsiloxane
PEC	Photoelectron chemical
PSI	Pollutant Standard Index
PTFE	Polytetrafluoroethylene
PV	Photovoltaic
PVC	Polyvinyl chloride
rGO	Reduced graphene oxide
RNA	Ribonucleic acid

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Air pollution has become a serious concern in recent years, with severe toxicological repercussions for human health and the ecology. There are two types of air pollution which are ambient pollution and indoor pollution. According to the World Health Organization (WHO), the six primary air pollutants that endanger human health and ecosystems are carbon monoxide (CO), lead (Pb), nitrogen oxide (NO_x), ozone (O_3), particle pollutants (PM) and sulphur dioxide (SO_2) (Ghorani-Azam, Riahi-Zanjani and Balali-Mood, 2016). The two approaches to address air pollution are prevention and removal. For the removal method, filtration and adsorption technologies such as high efficiency particulate air (HEPA) filters, electrostatic filters, air filtration and gas adsorption filtration are some of the most prevalent techniques applied. However, instead of removing pollutants completely, these techniques merely shift the pollutants to another phase, necessitating further disposal or handling stages (Zhao and Yang, 2003). As a result, there is a necessity to create an efficient, safe and low-cost method to decompose a broad spectrum of air contaminants (Ren et al., 2017).

Coronavirus disease (COVID-19) has become a significant global infectious disease at the start of 2020. COVID-19 is spread by coughing, sneezing or even talking by the infected individual. COVID-19 virus droplets may deposit and dry on various surfaces in specific circumstances and people are then infected by contacting the contaminated surface with their hands (Shirvanimoghaddam et al., 2021). Infected surfaces in public areas including hospitals, parks, public transit and schools are a well-known cause of infection epidemics (Campos et al., 2020). The virus has been found to survive on stainless steel and plastic surfaces for two to three days, four hours on copper, up to three hours in aerosols and twenty-four hours on cardboard (Gharaibeh, Smith and Conway, 2021a). A total of 3,790,505 deaths have been documented worldwide as of June 2021 (Worldometer, 2021). Covid-19 can be reduced on high-touch surfaces such as lift buttons, doorknobs and handrails by using a photocatalytic coating material such as titanium dioxide (TiO_2), zinc oxide (ZnO), silicon dioxide (SiO_2) and etc. When semiconductors come into contact with light, they can produce virus-killing radicals. They have significant photocatalytic capabilities and biocidal effects on germs, bacteria, fungi and viruses (Ruiz-Hitzky et al., 2020). In a recent paper published by Matsuura et al. (2021), demonstrated that the LED-TiO_2 photocatalytic reaction inactivated COVID-19 by RNA damage, virion membrane damage and viral protein degradation. It was capable of inactivating 99.9% of COVID-19 in aerosols within 20 minutes. In conclusion, photocatalytic reactions remove COVID-19 effectively.

Photocatalysis is referred to a chemical reaction that is accelerated by light. A photocatalyst is a chemical that initiates the process without participating in it. A photocatalyst coating uses photocatalysts as one of its constituents. To put it another way, it is analogous to photosynthesis, in which light energy is converted into chemical energy (Fujishima, Rao and Tryk, 2000). They are based on the production of electron and hole (e^--h^+) pairs of charge carriers in a semiconductor particle when photons of appropriate energy contact with it. The migrating holes oxidise hydroxyl groups bonded on the semiconductor surface to hydroxyl radicals ($^{\bullet}OH$). Electrons are consumed in the presence of oxygen (O_2), resulting in the production of superoxide radical anions ($^{\bullet}O_2^-$) (Bíbová et al., 2019). Equation (1.1) and (1.2) shows the reactions with O_2 and H_2O to form radicals. Following UV irradiation, the organic contaminants deposited on the TiO_2 surface undergo oxidative degradation and turn pollutants into harmless byproducts, CO_2 and H_2O. In addition, water is strongly attracted to TiO_2 surface. Water does not form droplets on the surface due to the attraction force; instead, it creates a sheet that undercuts the dirt by flushing it away and dries fast (Parkin and Palgrave, 2005).

$$O_2 + e^- \rightarrow {}^{\bullet}O_2^- \tag{1.1}$$

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+ \tag{1.2}$$

As cleaning glass and tile surfaces require a large amount of energy, chemical detergents and high cost, photocatalytic coating material has received a lot of attention due to their electrical structure, light absorption qualities, charge transport characteristics and excited-state lifespan (Ameta and Ameta, 2016). Photocatalysis has been touted as an excellent method for air purification. It has the potential to degrade a broad spectrum of contaminants into non-toxic or less dangerous forms under ambient conditions by utilising sun radiation (Escobedo and Lasa, 2020). Photosensitive semiconductors, such as TiO_2 absorb UV light and generate reactive hydroxyl radicals ($^{\bullet}OH$) in the presence of O_2 and H_2O. To mineralize pollutants into carbon dioxide and water, these free radicals undertake a sequence of processes that include bond breaking, substitution and electron transfer (Zhong and Haghighat, 2015). Self-cleaning technology has a wide range of uses, including washing glass windows and solar panels, as well as in industries such as textiles and cement factories. Their potential is enormous and their market is genuinely worldwide, thanks to their extensive applications in a variety of disciplines (Rafique et al., 2020). Based on their function, self-cleaning coatings are classified as hydrophobic and hydrophilic. Hydrophobic coating is also named "lotus effect" (Zhao et al., 2017). It achieves self-cleaning by causing water droplets to glide and roll across the surfaces and subsequently clean them with a contact angle (CA) greater than 90°. In contrast, a hydrophilic coating causes water to spread (sheeting of water) over the surfaces, carrying dirt and other impurities away when the contact angle is less than 90° (Ganesh et al., 2011).

1.2 Importance of the Study

Nowadays, the use of traditional air purification methods is frequently contrasted with the use of photocatalytic coatings. According to popular belief, photocatalytic coating provides additional benefits. The most notable feature is that photocatalytic coating is effective, affordable and environmentally benign (Li, Li and Zhou, 2020). The area of nanomaterials photocatalytic encompasses a wide range of applications such as self-disinfection, self-cleaning, CO_2 photoreduction, water and air treatment (Zhang et al., 2019). In fact, photocatalytic coating helps to improve quality of life (Hamidi and Aslani, 2019). However, the current usage of photocatalytic coatings is mostly employed in Japanese and European markets (Future Markets, 2014). Thus, photocatalytic coating should be introduced and used all over the world.

1.3 Problem Statement

Numerous pollutants in the air include halogen derivatives, volatile organic compounds (VOCs), hydrocarbons, fumes, mists, gaseous pollutants, polycyclic aromatic hydrocarbons (PAHs), smoke and dust can lead to many diseases. People who are exposed to air pollution suffer from numerous health problems. Effects are classified as either short-term or long-term. Infections such as bronchitis or pneumonia are examples of short-term effects. They can also cause irritation to the skin, nose, eyes or throat (National Geographic, 2021). It is well acknowledged that air pollution has long-term consequences on the onset of diseases such as respiratory infections, inflammation, cardiovascular dysfunctions and cancer. As a result, air pollution is related to millions of deaths each year around the world (Ghorani-Azam, Riahi-Zanjani and Balali-Mood, 2016).

Infections caused by bacteria and viruses can be mild, moderate or severe. The common cold is an upper respiratory tract viral infection that predominantly affects the nose and mouth. The common cold is a widespread respiratory ailment caused mainly by a virus (Lee et al., 2018). Bacterial infections have killed far over half of all humans who have ever lived on the planet. In the past, bacterial infections have caused significant pandemics, such as the bubonic plague, which has killed 50-60% of the population of Europe during the Black Death in the 14th Century (Lenz and Hybel, 2015). In addition, one of the biggest pandemics causes by virus is the 1918 "Spanish flu". It was estimated that 50 million people died. Mutations of Spanish Influenza known as Asian and Hong Kong Flu respectively erupted globally in 1957 and 1968, killing over 2 million people. In 2009, a new flu strain known as 'Swine Flu' spread throughout the globe, killing an estimated 575,500 people (Qadir, Malik and Kazmi, 2020).

Dust can adhere to the glass surface due to condensation and static charge attraction (Aranzabe et al., 2018). The buildup of dust and contaminants upon the cell surface, which serves as a deterrent between photovoltaic (PV) and irradiation, negatively impacts PV cell performance. The existence of comparatively high moisture in the air combined with dust can produce thin surface layers on the PV that is difficult to remove via wind or conventional cleaning methods, particularly in arid locations where water is scarce (Kazem et al., 2020). As a result, dust accumulation limits the amount of radiation that may be reflected and focused into the receiver, lowering the solar collector's optical reflectance and output power by 5% to 25% (Aranzabe et al., 2018). Corrosion is the degradation of metals caused by the reaction between corrosive components in the environment, such as Cl, F^-, CO_2 and O_2 (Abdeen et al., 2019). Corrosion has both direct and indirect consequences in our daily lives. Reinforcing steel bars in concrete can corrode behind the scenes and result in highway failure, electricity towers collapse, damage to buildings, bridges and car parks. Among other things, they are causing significant repair expenses and endangering public safety (ASM International, 2019). The National Association of Corrosion Engineers (NACE) conducted detailed research to determine costs within each sector relevant to all developed countries, revealing that Malaysia's annual cost of corrosion is around RM 600.0 billion, accounting for 4% of the country's GDP (Isa, Manaf and Anuar, 2018).

However, a practical application of photocatalysis for environmental goals has yet to be discovered. The TiO_2 photocatalytic coating has one significant flaw, which is it absorbs UV radiation lesser than 400 nm, which accounts for only about 3% of the electromagnetic spectrum that reaches the Earth (Bogdan et al., 2015). The second drawback of photocatalysis that makes it impractical for air purification is fouling or deactivation (Weon, He and Choi, 2019). Therefore, significant work has been put into solving these difficulties over the last few decades, such as metal/non-metal doping, semiconductor heterostructure formation, dispersal onto large surface area substrates, metal deposition and carbon-based material loading. The methods described above aid in improving electron and hole separation as well as extending light absorption into the visible range (al Jitan, Palmisano and Garlisi, 2020). For example, doping TiO_2 with a range of metal ions, such as transition metal and rare earth metal ions (Kang et al., 2019). The Schottky barrier produced at the metal-TiO_2 interface has been shown to effectively delay e^--h^+ recombination when metal nanoparticles with a significant work function, such as Ag, Pt and Au, are deposited onto TiO_2 surfaces. Charge carrier recombination is reduced, resulting in increased photoactivity. The metal nanoparticles serve as a bridge between the TiO_2 surface and an acceptor, storing and transporting photogenerated electrons (Dong et al., 2015).

Filtration and adsorption are two traditional air cleaning purification. However, both have significant disadvantages. For example, particulate pollutants will deposit on the filter bed and the filter's surface of high efficiency particulate air (HEPA) filters. Eventually, filter cake forms on the filter's surface after a period. The resistance increases exponentially as the particulate matter deposits. As a result, the usage of wind turbines and their energy consumption is increasing. Thus, the filter media material must change regularly to decrease energy usage. Furthermore, the filter material is a one-time use item that is not cost effective (Collum, 2017). Besides, electrostatic (ES) air purifiers major disadvantage is that it uses high-voltage electricity to ionise oxygen in the air and creates secondary pollutants. Ozone concentration created by ES air filters easily surpasses the indoor average of 0.16 mg/m^3 for one hour, in accordance with the National Indoor Air Quality Standard (GB/T 18883-2015) (Deng and Zhang, 2018). On the other hand, the limitation of activated carbon adsorption is that the adsorption carrier must be changed once it becomes saturated and cannot be recycled. This had led to high maintenance costs (Soni, Bhardwaj and Shukla, 2020). Table 1.1 summarizes the disadvantages of filtration and adsorption.

Table 1.1: Disadvantages of Different Conventional Air Purification

Conventional Air Purification	**Disadvantages**	**References**
High efficiency particulate air (HEPA) filters	• Filter replacement might be costly. • Allergens, germs, viruses and airborne compounds are not captured by HEPA filters since they are smaller than 0.3 micrometres. • HEPA is characterised by a significant pressure drop, which raises the operational cost. • HEPA filter is fragile. It must be delivered, stored and handled like delicate equipment.	Liu et al., 2017; Dey, Choudhary and Ghosh, 2017
Electrostatic (ES) air filters	• Back-corona discharge. • Particle re-entrainment into the air. • Release ozone as its by-product.	Altun and Kilic, 2019
Activated carbon adsorption	• Filter change is required. It may become inconvenient and costly. • Expensive raw material. • Problems with saturating regeneration. • Mineral processing is not efficient because resistance is higher.	Soni, Bhardwaj and Shukla, 2020; Liu et al., 2017

1.4 Aim and Objectives

The study's goal was to examine the existing use of photocatalytic coating for air purification and self-cleaning, its practicality and effectiveness and sketch out the future prospects for photocatalytic coating for air purification and self-cleaning.

The following are the research's objectives:

(i) To review the applications of the photocatalytic coatings for air purification and self-cleaning.

(ii) To suggest future perspectives and limitation in current field of research.

1.5 Scope and Limitation of the Study

The application of photocatalytic coating in air purification and self-cleaning was the exclusive focus of this study. Although photocatalytic coatings may be used in various applications, including self-sterilization and anti-fogging, this research did not examine these topics. Most recent discoveries and developments in photocatalytic coating have concentrated on the principal theme of air purification and self-cleaning. In addition, photocatalytic coating's future prospects were discussed regarding how it may be used for air purification and self-cleaning.

The real experiment could not be carried out due to the COVID-19 pandemic. As a result, the research was carried out by evaluating the literature on photocatalytic coatings for air purification and self-cleaning.

CHAPTER 2

LITERATURE REVIEW

2.1 Air Pollution

The existence of harmful chemicals or pollutants, particularly those of biological origin, in the atmosphere at hazardous levels to one's health is referred to as air pollution. In a broader sense, air pollution refers to the existence of chemicals or compounds in the air that are not usually present and reduces air quality or creates adverse changes in quality of life, including damaging the ozone layer or causing global warming (Stanek and Brown, 2019). Pollutants can be grouped into primary or secondary. Primary pollutants are emitted into the atmosphere directly from their sources. In contrast, secondary pollutants are not released directly from sources but instead generated in the atmosphere from primary pollutants, also known as precursors. Examples of primary pollutants are carbon dioxide (CO_2), particulate matter (PM), carbon monoxide (CO), volatile organic compounds (VOCs), sulphur oxide (SOx) and nitrogen oxide (NOx). Ozone (O_3), nitric acid (HNO_3), nitrogen dioxide (NO_2) and organic aerosols are categories under secondary pollutants (Daly and Zannetti, 2007).

2.1.1 Particle Pollutants (PM)

Particulate matter is defined as any liquid or solid that is so finely split that it may be windblown or suspended in air or gas (Rogoff and Screve, 2011). Particles are classified based on aerodynamic diameter, which influences particle deposition along airways (Yammine and Latzin, 2020). $PM_{2.5}$ refers to fine particles with nominal dimensions of 2.5 µm or less. $PM_{10-2.5}$ denotes coarse particles with nominal sizes between 2.5 and 10 µm, whereas PM with nominal diameters less than 0.1 µm is referred to as ultrafine particles (Stanek and Brown, 2019). Smoke, dust, aerosols, metallic oxides and pollen are all examples of PM, which can be solid or liquid (Daly and Zannetti, 2007). Sources of PM are both natural and man-made. A variety of natural sources contribute millions of tonnes of PM to the atmosphere. Volcanic eruptions, forest fires, salt spray, rock debris, wind and dust storms, interactions between gaseous emissions and soil erosion are examples of natural causes. Artificial activities such as coal combustion and agricultural trash, petroleum foundries, industrial processes, steel industry, fuel combustion, fly-ash emissions from power plants, smelting and mining operations all contribute to PM levels in the environment (Ukaogo, Ewuzie and Onwuka, 2020). The respiratory system is the first line of defence against air contaminants before they enter the circulatory system and other areas of the body. The size of the particle determines which parts of the respiratory system are impacted. PM_{10} affects the upper respiratory tract, whereas ultrafine particles impact the lung alveoli (0.1 µm diameter). Particulate particles entering the respiratory tract can stimulate and erode the alveolar wall, causing respiratory damage, impairing lung function and increasing the occurrence of respiratory symptoms. Finer particles are more detrimental to human health than coarser particles when it comes to mortality, pulmonary and cardiovascular consequences. Particulate matter can cause premature death in individuals with lung or heart illness, nonfatal heart attacks, worsen asthma, impair lung functioning, irritate airways, induce coughing and difficulty breathing and so on (Huang, Liu and Guo, 2018; el Morabet, 2019).

2.1.2 Nitrogen Oxide (NOx) and Sulphur Dioxide (SO_2)

Nitrogen oxide (NOx) is a class of highly reactive gases formed by nitrogen (N_2) interaction with oxygen (O_2) (Brusseau et al., 2019). It has the chemical formula of NOx. It exists in three forms: nitrogen dioxide (NO_2), nitric oxide (NO) and nitrous oxide (N_2O) (Beig et al., 2017). In the presence of air and ultraviolet radiation (UV) from sunlight, NO_2 interacts to create ozone and nitric oxide (NO). The NO then interacts with free radicals in the environment, produced when UV rays interact with volatile organic molecules (VOCs). NO is subsequently recycled to NO_2 by the free radicals. As a result, each NO molecule can generate ozone several times (United State Environmental Protection Agency (EPA), 1999). Tropospheric ozone has been and continues to be a significant source of air pollution globally and it is the principal component of smog. Tropospheric ozone is ozone in the atmosphere that humans breathe. High-temperature combustion processes, such as those found in cars and power plants, are the primary drivers of anthropogenic NOx emissions. Furthermore, biogenic or natural sources include lightning, forest fires, grass fires and trees, which are also nitrogen oxide sources (Miller, 2005). NOx has a wide range of health and environmental effects due to the family of nitrogen oxides' numerous components and derivations, including nitrates (NO_3^-), nitric acid (HNO_3), nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2). HNO_3 vapour and associated particles are formed when NOx reacts with ammonia, moisture and other substances. Concerns about human health include impacts on breathing and the respiratory system, lung tissue destruction and early mortality. Small particles can penetrate deeply into sensitive areas of the lungs, causing or worsening respiratory diseases, including emphysema and bronchitis, as well as aggravating pre-existing heart disease. Furthermore, it has the potential to contribute to global warming. Nitrous oxide (N_2O), a NOx family member, is a greenhouse gas. It builds up in the atmosphere alongside other greenhouse gases, causing the earth's temperature to rise gradually. This will increase hazards to human health, sea-level rise and other negative changes to plant and animal habitat. When NOx and sulphur dioxide combine with other chemicals in the air, they produce acids that fall to the ground as rain, fog, snow or dry particles. Some may be transported hundreds of kilometres by the wind. Acid rain degrades forests, houses, historical sites and makes lakes and streams acidic that is unsuitable for many aquatic species (Environmental Protection Agency (EPA), 1998; Frampton et al., 2002; Antipova, 2020).

Sulphur dioxide (SO_2) is a frequent component of urban air pollution (Doty, 2015). SO_2 may be found in both gas and liquid forms (MD, 2007). SO_2 is a colourless molecule that has an oppressive and pungent odour. The burning of sulphur-containing fuels, such as oil and coal, is the primary source of SO_2 (Daly and Zannetti, 2007). In the past, sulphur dioxide air pollution disasters have been linked to an increase in death rates among patients with chronic lung disease and the elderly. At concentrations of 6–10 ppm, acute irritation of the eyes and nasopharynx has been recorded. High levels of exposure (50 ppm) cause damage to the larynx, trachea, bronchi and alveoli (S.Newman and E.Stinson, 2008). Patients first suffer a burning sensation in their eyes, nose and throat together with coughing, chest discomfort, chest tightness and dyspnea, as well as conjunctivitis, corneal burns and pharyngeal edema, followed by pulmonary edema hours later. After two to three weeks of exposure, bronchiolitis obliterans might appear (Gammon, Moore and O'Malley, 2010). Sulfurous acid, produced when sulphur dioxide reacts with water, is the most dangerous type of sulphur dioxide. Because sulphurous acid is highly lipid-soluble and quickly penetrates the corneal epithelium, it is more hazardous than sulfuric, hydrochloric or phosphoric acids (S.Newman and E.Stinson, 2008).

2.1.3 Volatile Organic Compounds (VOCs)

As we go about our everyday lives, we come into contact with volatile organic compounds (VOCs). VOCs are organic chemicals that rapidly form vapours at room temperature and thus emit gases from certain solids or liquids. VOCs can also be described as chemicals with high vapour pressure and poor water solubility (Thurston, 2017). VOCs are a type of liquid organic compound that has varying lipophilicity and volatility (Anand, Philip and Mehendale, 2014). Carbon is found in all organic compounds. Organic compounds are the fundamental chemicals of all living things. Today, most organic molecules in the atmosphere are artificial rather than naturally occurring. Aside from combustion, VOCs may be found in glues, gasoline, paints, industrial chemicals (principal dry cleaning solvent) and other products used at home or work (United States Environmental Protection Agency, 2020). The chemical structure or functional group of VOCs is used to classify them. Over a hundred VOCs have been discovered, including hazardous chemicals such as chloroform, formaldehyde, acetaldehyde, benzene, toluene, xylene, styrene and certain essential oil constituents (Tisserand and Young, 2014). Indoor air is dominated by toluene and benzene, whereas chloroform ($CHCl_3$) is the most common in water (Anand and Mehendale, 2005).

Some VOCs are beneficial in terms of ozone layer formation but the vast majority of VOCs are harmful to the environment. One of the damages to the environment caused by VOCs is that they encourage smog formation. VOCs are a significant contributor to smog. Nitrogen oxide (NO_2) combines with VOCs from vehicles and other industrial operations to create ozone (Durkee, 2008). The interaction between ozone and nitrogen oxide produces tiny particles in the atmosphere. This combination of tiny particles, ozone and other pollutants leads to smog formation, which may be highly hazardous, particularly on cold days

(United States Environmental Protection Agency, 2015). Aside from reducing vision, smog can have severe consequences for the human body. Smog may irritate eyes, nose, throat and develop and aggravate respiratory illnesses such as asthma. For more severe cases, lung tissue might be permanently damaged and cause significant harm to the immune system if constantly exposed to pollution (Yang, Hoffmann and Scheffran, 2017). Most VOCs are generated spontaneously from natural sources such as plants. Oceans and human activities are other vital sources of VOCs. These VOCs contribute to greenhouse gas emissions. Whilst VOCs have a minor impact on world average temperature than direct greenhouse gases like carbon dioxide. In a nutshell, VOCs contribute to global warming (Murrells and Derwent, 2007). VOCs are responsible for a wide range of health issues. Since inhalation is a significant route of exposure due to its smaller molecular size and absence of charge, it may be quickly absorbed by the lungs, gastrointestinal (GI) tract and skin (Anand, Philip and Mehendale, 2014). Some of the VOCs may have both short and long-term negative health consequences. Eye irritation, headache, allergic skin reaction, nausea, dizziness, nose and throat pains are common indications or symptoms of VOC exposure. VOCs have been linked to sick building syndrome. According to recent research, VOCs have been shown to cause cancer in animals and some are suspected or proven to cause cancer in people, even at extremely low doses (Garcia-Jares, Barro and Llompart, 2019).

2.2 Air Regulations and Guidelines

In Malaysia, ambient air quality is monitored using the Air Pollutant Index (API). The Air Pollutant Index (API) is a measure of the air quality in a specific location. The API value is determined by averaging the concentrations of air pollutants SO_2, NO_2, CO, O_3, $PM_{2.5}$ and PM_{10}, respectively. This score indicates the current state of air quality and its implications on human health. Index value ranges can be classed as good, moderate, unhealthy, extremely unhealthy and hazardous. Malaysia's API system closely resembles the US Environmental Protection Agency's (US-EPA) Pollutant Standard Index (PSI) (DOE Malaysia, 1997).

The Malaysian Ambient Air Quality Guideline, which had been in use since 1989, was replaced by the New Malaysia Ambient Air Quality Standard.

The air pollution concentration limit was being steadily tightened until 2020. Intermediate target 1 (IT-1) was established in 2015, interim target 2 (IT-2) was scheduled in 2018 and full implementation of the standard was set in 2020. The overview of three interim targets from 2015 to 2020 is shown in Table 2.1.

Environmental Quality Act of 1974 and Clean Air Regulation of 2014 are legal laws and regulations in Malaysia to reduce air pollution. Environmental Quality Act of 1974 went into effect on 15th April 1975. This Act is pertaining to prevention, reduction, control of pollution, enhancement of the environment and related purposes. Part III outlines the steps required to acquire a permit from the Director-General of Environmental Quality (Government of Malaysia, 1974). Clean Air Regulations 2014 supersedes the Environmental Quality (Clean Air) Regulations 1978 and the Environmental Quality (Dioxin and Furan) Regulations 2004. It was gazetted on 4th June 2014 and went into effect on 5th June 2014. Clean Air Regulations 2014 seeks to control air pollutant emissions from industrial operations such as power plants, waste fuel facilities and asphalt mixing plants (Diyana, n.d.).

Table 2.1: New Malaysia Ambient Air Quality Standard (DOE Malaysia, 2020)

Pollutants	**Averaging Time**	**Ambient Air Quality Standard** IT-1 (2015) µg/m³	IT-2 (2018) µg/m³	Standard (2020) µg/m³
Particulate Matter with the size of less than 10 micron (PM_{10})	1 Year	50	45	40
	24 Hour	150	120	100
Particulate Matter with the size of less than 2.5 micron ($PM_{2.5}$)	1 Year	35	25	15
	24 Hour	75	50	35
Sulfur Dioxide (SO_2)	1 Hour	350	300	250
	24 Hour	105	90	80
Nitrogen Dioxide (NO_2)	1 Hour	320	300	280
	24 Hour	75	75	70
Ground Level Ozone (O_3)	1 Hour	200	200	180
	8 Hour	120	120	100
*Carbon Monoxide (CO)	1 Hour	35	35	30
	8 Hour	10	10	10

*mg/m³

2.3 Air Purification

Many forms of air filtration are used to address air pollution, including High Efficient Particulate Air (HEPA) filters, electrostatic (ES) filters and activated carbon filters (ACF).

2.3.1 High Efficient Particulate Air (HEPA) Filters

The term "HEPA" refers to a type of pleated mechanical air filter. According to the official definition by the United States Department of Energy (DOE), the term "HEPA" is an abbreviation for high efficiency particulate air filter (United States Environmental Protection Agency, 2019). High efficient particulate air (HEPA) filters were created in the early 1940s and were originally employed by the Manhattan Project to control the spread of radioactive pollutants in the air. When compared to modern HEPA filters, the early filters were huge and ineffective. Some included asbestos fibres. HEPA filter technology was published after World War II and commercial production began in the 1950s (Avery, 2001). HEPA filters were commercially launched to remove viruses, germs, airborne fungus, allergen, human hair and particulate pollutants from building air, including pet dander, soot particles and dust (Encyclopaedia Britannica, 2015). This sort of air filter can potentially remove 99.97% of dust, pollen, mould, germs and any other airborne particles larger than 0.3 µm. The most penetrating particle size (MPPS) for HEPA filters are particles with a diameter of 0.3 microns (United States Environmental Protection Agency, 2019). Figure 2.1 shows HEPA filters that are commonly found in current markets.

Three important variables combine to make HEPA filters effective. To begin, one or more exterior filters act as sieves, trapping bigger particles of dirt, dust and hair. Follow by a concertina, a mat of incredibly thick threads inside the filters that catch tiny particles. These pre-filters are meant to filter out 90% of the particles in the entering air. Three separate processes are used in the inner section of the filter to capture particles as they pass through in the flowing air stream. Some particles are captured and trapped when they smash into the threads at high air speeds, while the fibres catch others as the air passes by. Particles tend to wander more randomly through the filter at lower air speeds by Brownian motion and may cling to the fibres as they do so. These three processes work together to allow HEPA filters to collect particles that are both bigger and smaller than a predetermined size (Sandle, 2013).

Figure 2.1: HEPA Filter (Avery, 2001)

2.3.2 Electrostatic (ES) Filters

Electrostatic (ES) filters are a type of air-cleaning equipment that is electrically linked and designed to remove particles from airstreams (NIOSH, 2003). An ES filter is also known as a washable air filter that combines electrostatics and filtration (Liu et al., 2017). These filters capture air particles by utilising oppositely charged ions. These filters have many metal or synthetic material layers, which generate a static charge when air flows past them. As a result, when air enters the filter for the first time, a mesh layer positively charges its particles. As these positive particles go further through the filter, they are attracted by negatively charged layers. Thus, dust and other pollutants become encrusted on the filter's surface. There are numerous positively and negatively charged layers in electrostatic filters. As a result, once the initial few particles are caught, another layer generates a positive charge in the air. Following that, another negatively charged layer effectively traps the contaminants and so on for numerous layers until the majority of the dust is filtered out (Peamthong and Larsen, 2010; Afshari et al., 2020; Leung and Sun, 2020). ES filters can be classified into two types. One type of ES filter is electrostatically charged filter media, while another type is electrostatically precipitator (NIOSH, 2003).

ESP is a type of air filter that employs electrostatic charge to remove dust particles. By delivering a high voltage to the electrodes, ESP ionises the air. Ionised air charges dust particles, which are then collected on oppositely charged collecting plates. Because ESP actively eliminates dust and smoke from the gas, it is suitable for a broad range of biomass, including wood and low-quality coal, all of which create a lot of smoke. Furthermore, ESPs often have collection efficiency, the ratio of particle counts entering and leaving the filter greater than 99%. It is feasible to create a flexible low-power ESP air cleaner with the proper design strategy (Park, 2017). Figure 2.2 depicts the schematic diagram of electrostatic filters. ESP can be divided into two portions. The first portion is the ionising section, which is made up of a succession of tiny wires charged to up to 13 kV and alternatively inserted with earthed rods. This causes a corona discharge and the airborne particles get a positive electrostatic charge as they travel through the ionising field. The collector section is the second component and it is made up of a sequence of parallel, vertical steel plates with a voltage differential of 6–7 kV between consecutive plates. The ionised dust particles are drawn to these plates and attach to them. Oil is occasionally applied to the plates to aid with dust retention. The filters are washed with high-pressure water to clean them automatically (Legg, 2017; Praneeth et al., 2017).

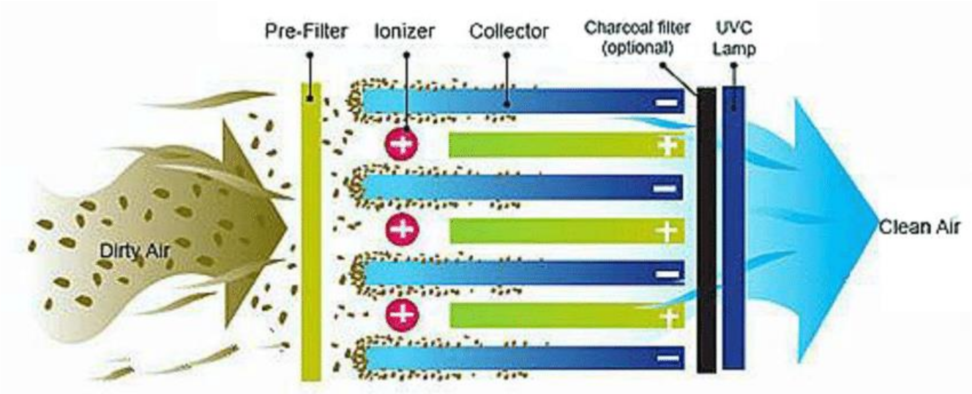

Figure 2.2: Schematic Diagram of Electrostatic Filter (Liu et al., 2017)

2.3.3 Activated Carbon (AC) Filters

The Japanese created activated carbon filters (ACF) in the 1970s using rayon, polypropylene nitrile as raw ingredients. Due to its big adsorptive capacity, ease of regeneration, fast stripping speed, more efficient absorption pore, rich form, short adsorption trip and uniform pore size distribution, ACF is regarded as one of the most excellent air purification materials in the 21st century (Liu et al., 2017). Granular activated carbon (GAC), powdered activated carbon (PAC), woven carbon filter and treated carbon are the most popular ACF used in air purifiers. GAC is made up of big granules with a diameter of 3 mm, around the size of tiny pebbles or sand. GAC filters have a long service life and can be combined with other substances such as zeolite. They are very effective in removing odours and gaseous pollutants such as formaldehyde (Lu et al., 2020). Secondly is PAC. PAC is made up of granules ranging in size from 10 to 50 microns. These grains are resin-bonded together to form a single big block. This filter has a faster and greater adsorption capacity than its GAC due to the smaller particles (Sung et al., 2019). Next is woven activated filters. Activated carbon is woven into rayon fibre to make a fabric with woven carbon filters. This air cleaner appears in an air purifier as a thin sheet of carbon filter. It may also be available as a stand-alone device attached to locations requiring purification, such as diaper disposal containers or kitchen waste bins (Tharewal, Landage and Wasif, 2013). Finally, treated carbon, also known as impregnation. In a procedure called impregnation, carbon is sometimes treated with potassium permanganate or silver to improve its adsorption ability. Impregnated filters are capable of removing a wider variety of chemical gases, including natural gas and formaldehyde (Hu et al., 2018).

ACF uses physical adsorption (physisorption) and chemical adsorption (chemisorption) to remove gaseous pollutants from airstreams. Physisorption is the adsorption of gaseous pollutants onto solid porous materials by Van der Waals interactions (nuclear attraction) and contraction in the tiny pores. Because of the comparatively modest forces, this is a reversible process, where gases that have been adsorbed can subsequently desorb back into the airstream (Lyngby et al., 2015). The activated carbon in carbon air filters is a very porous material. A typical gramme of activated carbon has a surface area of $1000m^2/g$. According to Liu et al. (2020), the greater the surface area it has, the higher chance activated carbon has of capturing molecules. Carbon is a lattice of carbon atoms that are interconnected. The method through which activated carbon air purifies remove pollutants from the air is known as adsorption. Adsorption is the process by which contaminants adhere to the exterior of the carbon (Sweetman et al., 2017). When air passes through a carbon filter, all of the molecules in the air pass through as well. The molecules pass through the activated carbon as they travel through the filter. Some molecules become trapped in the carbon as a result of the adsorption process. Adsorption occurs when a particle adheres to the surface of a substance. This is a crucial idea to grasp when dealing with carbon filters. As mentioned earlier, the greater the accessible surface area, the more likely a particle will become attached to the carbon filter (Rodríguez-Reinoso, 2001).

2.4 Photocatalysis

The field of chemistry dealing with the chemical effects of light is known as photocatalysis. A photocatalyst is a material that absorbs light to increase its energy level and then transfers that energy to a responding substance to cause a chemical reaction. There are several materials with photocatalytic capacity, with TiO_2 being the most efficient. Superoxide anion is formed when a negative electron interacts with an oxygen molecule. Positive holes are produced in the valence electron band when the photocatalyst absorbs light and reacts with electrons. Positive holes in TiO_2 react with H_2O or dissolved O_2 to produce OH radicals, which degrade hazardous compounds. It does not require any unique energy and operates only on clean energy in everyday life. Titanium dioxide has a high photocatalytic reaction. It has a high oxidation and breakdown resistance (Oshida, 2013; Yadav, Kim and Pawar, 2016).

Giacomo Ciamician, an Italian scientist, was the first to perform experiments to determine whether "light and light alone" might induce chemical reactions as early as 1901. He conducted experiments with blue and red lights and discovered that only blue light produced a chemical impact. He was cautious enough to rule out the idea that these reactions were fueled by light-induced thermal heating. The term "photocatalysis" is a mixture of Greek terms and is made up of two parts which are the photo (phos) for light and catalysis (katalyo) for decomposition or degradation. In 1911, the word "photocatalysis" arose for the first time in scientific literature. The term was coined by German scientist Dr. Alexander Eibner, who used it in his study on the effects of zinc oxide (ZnO) light on the bleaching of the dark blue pigment, Prussian blue (Zhu and Wang, 2017a; Ahmad, Ghatak and Ahuja, 2020). Later, in 1972, Fujishima and Honda used an n-type semiconductor TiO_2 anode paired with a platinum (Pt) cathode and proved the possibility of photoelectron chemical (PEC) water splitting under UV irradiation (Zhang et al., 2016). The idea of turning solar energy into chemical energy was highly appealing. Therefore, many scientists committed their time and effort to photocatalytic research. Since then, researchers have undertaken extensive studies on TiO_2 and other photocatalysts, with the goal of better understanding the fundamental principles of photocatalysis, increasing photocatalytic efficiency and broadening the spectrum of photocatalytic systems and applications (Long et al., 2020). In 1994, metal ion-doped TiO_2 thin films were discovered, followed by superhydrophilic TiO_2 films in 1997, anion doped TiO_2 thin films in 2001 and visible light sensitive TiO_2 thin films in 2002 (Nurhasni, 2012).

TiO_2-based photocatalytic products were first commercialised in Japan in the mid-1990s (Fujishima and Zhang, 2006). Using the photocatalytic reaction of TiO_2, several applications have been developed, including self-sanitising surfaces, self-cleaning coatings, reduction of indoor air pollution and sick building syndrome, reduction of air pollution and wastewater treatment (Chen and Poon, 2009). For example, nano-TiO_2 self-cleaning coatings improve building upkeep, particularly for skyscrapers, by reducing the need for costly surface cleaning. TiO_2 may be applied to various surfaces to make them self-cleaning in both sunshine and room light (Future Markets, 2014).

2.4.1 Mechanism of Photocatalysis

A semiconductor has an electrical structure that consists of a conduction band (CB) and a valence band (VB) separated by an energy bandgap (E_g), which acts as an energy barrier for electrons. Irradiating the catalyst with photons with energies (*hv*) equal to or higher than its bandgap promotes an electron from the VB to the CB, resulting in the formation of the electron-hole pair (e_{cb}^{-} –h_{vb}^{+}). The photoelectrons' reduction potential is defined by the lowest energy level of the CB, whereas the photoholes' oxidising power is determined by the highest energy level of the VB. In the absence of appropriate electron and hole scavengers, the supplied energy is lost via heat by recombination in a matter of nanoseconds. The photocatalytic mechanism is depicted schematically in Figure 2.3. The photonic excitation of the catalyst is the first stage in the activation of the photocatalytic process and the following key phases reflecting the photocatalytic processes are shown below (Molinari et al., 2017).

1. Excitation of the catalyst

$$TiO_2 + hv \rightarrow e^- + h^+ \quad (2.1)$$

2. Adsorption on the catalyst surface

$$Ti^{IV} + H_2O \rightarrow Ti^{IV} - H_2O \quad (2.2)$$

$$Ti^{IV} + OH^- \rightarrow Ti^{IV} - OH^- \quad (2.3)$$

$$\text{Catalyst site} + S_1 \rightarrow S_{1ads} \quad (2.4)$$

3. Electron and hole trapping

$$Ti^{IV} + e^- \rightarrow Ti^{III} \quad (2.5)$$

$$Ti^{IV} - H_2O + h^+ \rightarrow Ti^{IV} - OH^{\cdot} + H^+ \quad (2.6)$$

$$Ti^{IV} - OH^- + h^+ \rightarrow Ti^{IV} - OH^{\cdot} \quad (2.7)$$

$$S_{1ads} + h^+ \rightarrow S_{1ads}^{+} \quad (2.8)$$

$$Ti^{III} + O_2 \rightarrow Ti^{IV} - O_2^{\cdot -} \quad (2.9)$$

4. Recombination of electron-hole pairs

$$e^- + h^+ \rightarrow \text{heat} \quad (2.10)$$

These holes and electrons may undertake repeated oxidation and reduction processes with almost any molecule deposited on the semiconductor's surface to produce the required products (Chatterjee and Dasgupta, 2005). The presence of water on the photocatalyst surface is alluded to as "absorbed water." This water is oxidised by positive holes formed in the valence band as a consequence of electrons moving toward the conduction band due to light irradiation, allowing hydroxyl (OH) radicals to form (agents which have strong oxidative decomposing power). Following that, these hydroxyl radicals react with contaminants in the air. In this instance, the pollutants eventually decompose, yielding carbon dioxide and water. Contaminants can react directly with the positive holes in such conditions, resulting in oxidative breakdown. Due to the fact that oxygen is a readily reducible material, it is used as an alternative to hydrogen production. Superoxide anions are formed when conduction band electrons combine with dissolved oxygen species. These superoxide anions bind to the oxidative reaction's intermediate products. This lowers carrier recombination while increasing photocatalytic activity (Saravanan, Gracia and Stephen, 2017).

$$Ti^{IV} - OH^{\cdot} + S_{1ads} \rightarrow Ti^{IV} + S_{2ads} \quad (2.11)$$

$$OH^{\cdot} + S_{1ads} \rightarrow S_{2ads} \quad (2.12)$$

$$Ti^{IV} - OH^{\cdot} + S_{1} \rightarrow Ti^{IV} + S_{2} \quad (2.13)$$

$$OH^{\cdot} + S_{1} \rightarrow S_{2} \quad (2.14)$$

$$O_2 + e^{-} \rightarrow O_2^{\cdot -} \quad (2.15)$$

$$M^{n} + e^{-} \rightarrow M^{(n-1)} \quad (2.16)$$

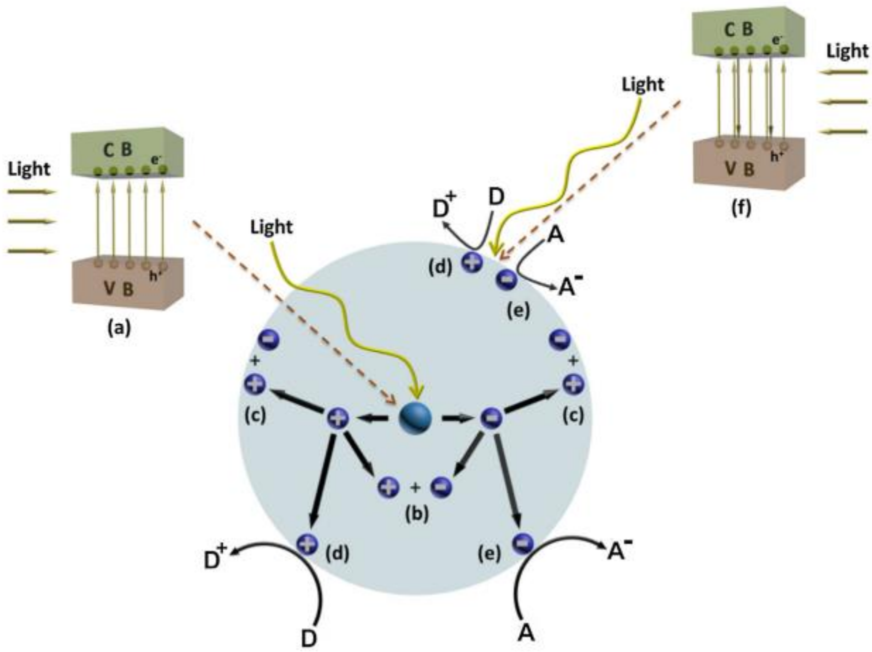

Figure 2.3: Schematic Diagram of Photocatalytic (Ren et al., 2017)

2.5 Self-cleaning

Several technologies are taken from natural examples. Self-cleaning technology is one of them. Butterfly wings, lotus leaves, gecko feet, cabbage and water strider legs are examples of self-cleaning surfaces found in nature (Rafique et al., 2020). Photocatalytic self-cleaning is the most often employed nano-function in building construction, with Japan leading the way. Because of the wide variety of potential uses, from window glass and cement to textiles, this function is used in a large number of structures of various sizes all over the world. Photocatalytic self-cleaning main action is to minimise the amount of dirt adherence on surfaces significantly. As a result, fewer detergents are used, reducing environmental contamination and material wear and tear. Reduced cleaning cycles also result in lower staff expenses and the fact that dirt attaches less implies that it is easier to remove. In general, photocatalytic self-cleaning is a low-maintenance and trouble-free option (Birkhäuser Basel, 2008).

Self-cleaning coatings are classified into two types: hydrophobic and hydrophilic. Both of these coatings clean themselves using water. The hydrophobic surfaces do this by rolling droplets, whereas the hydrophilic surfaces accomplish this by distributing water, which sweeps away debris. Titania-based hydrophilic coatings have the added benefit of being able to dissolve absorbed dirt under sunlight via photocatalysis (Ameta and Ameta, 2016). Surface wettability is determined by the structure's chemical composition and shape. Water generates an angle when it moves. The contact angle (CA) created between the three boundary surfaces (solid, liquid and vapour) determines the self-cleaning. A hydrophilic surface has a water contact angle (CA) of less than 90° between the liquid and solid surfaces, while a superhydrophilic surface has a CA of less than 50°. On a hydrophilic surface, the water spreads out and creates a thin layer (Surekha and Sundararajan, 2014). In contrast, the self-cleaning effect of hydrophobic coatings is due to their high water contact angles, which has a CA larger than 90° between the liquid and solid surfaces. Water on these surfaces creates almost spherical droplets that easily roll away, bringing dust and debris with them. Dirty water that falls over the hydrophobic coating is removed before it has a chance to dissipate. The rolling action cleans the surface more efficiently and leaves less debris than the sliding motion at lower contact angles. If the CA is zero, the surface is said to be ultrahydrophilic, but if the CA is more than 150°, the surface is said to be ultrahydrophobic (Parkin and Palgrave, 2005; Rafique et al., 2020). Figure 2.4 shows the basic process of self-cleaning.

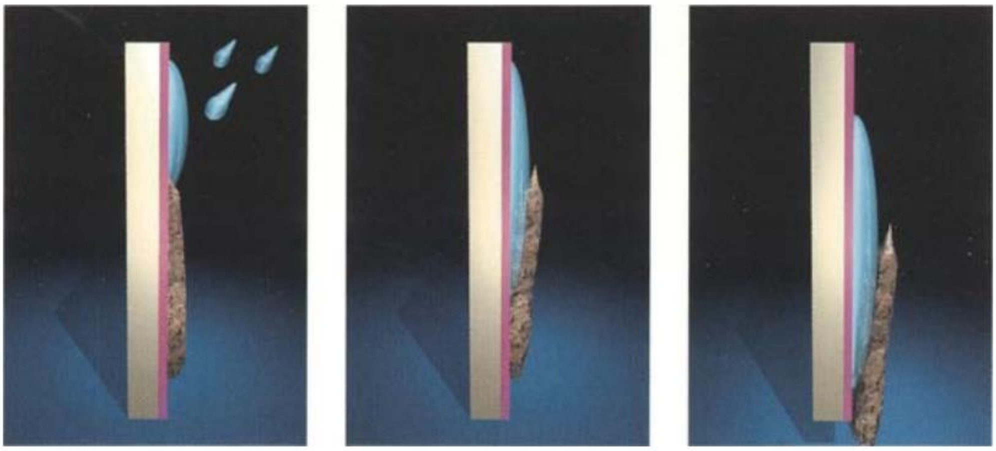

Figure 2.4: Basic Process of Self-cleaning (Birkhäuser Basel, 2008)

Surface coatings on solid substrates novel materials interactions. Interface evolution, surface adhesion, spreading and wettability characteristics should all be considered. A solid's wettability by a liquid is determined by the angle of contact between the liquid and the solid. The contact angle (CA) is determined by balancing interfacial forces and is described by Young's equation (Surekha and Sundararajan, 2014). Young's equation is a formula established by the English physicist Thomas Young in 1805 that defines the link between the surface tension, contact angle, interfacial tension between a liquid and a solid surface and the solid's surface free energy (Roura and Fort, 2004).

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \tag{2.17}$$

The interfacial tensions denoted as γ indicate equilibrium values at the intersection of three phases. The *sv*, *sl* and *lv* are the interfacial energies between the solid-vapour, solid-liquid and liquid-vapour phases (Ebnesajjad, 2011). The term θ is the solid surface's intrinsic contact angle. Figure 2.5 shows the equilibrium contact angle of an ink drop on an ideal surface. The equation serves as the foundation for further research on wettability. The vertical component of gravity and the liquid's surface tension are omitted in the equation and experiments had proven that they might be ignored. Low contact angle values implies that the liquid spreads evenly across the surface, whereas high contact angle values suggest that the liquid spreads poorly. The condition $\theta < 90°$ shows that the liquid has wetted the solid and the surface is considered nonwetting with liquid if the contact angle is $\theta > 90°$, with the limits of $\theta = 0°$ and $\theta = 180°$

indicating complete wetting and complete nonwetting, respectively (Surekha and Sundararajan, 2014; Polini and Yang, 2017). On the other hand, Young's equation is only applicable to smooth surfaces. However, the actual surface has some surface roughness. Therefore, a perfectly smooth surface does not exist. In 1936, Wenzel published the rough surface contact angle equation. The liquid droplet is assumed to infiltrate the gap on the solid surface thoroughly and its expression is as indicated in equation (2.18).

$$\cos\theta_w = r\frac{\gamma_{sv}-\gamma_{sl}}{\gamma_{lv}} = r\cos\theta \qquad (2.18)$$

The theoretical value of Wenzel's contact angle denoted as θ_w and r is defined as the ratio of the actual solid-liquid contact area to the predicted area (Shaoxian and Shizhu, 2019). According to Wenzel's relation, illustrated in equation (2.18), if a liquid's intrinsic contact angle on a solid surface is less than 90°, it is known as hydrophilic, further 'roughening' the interface will lower the effective contact angle. Similarly, when surface roughness rises, the contact angle of a hydrophobic surface increases (Surekha and Sundararajan, 2014).

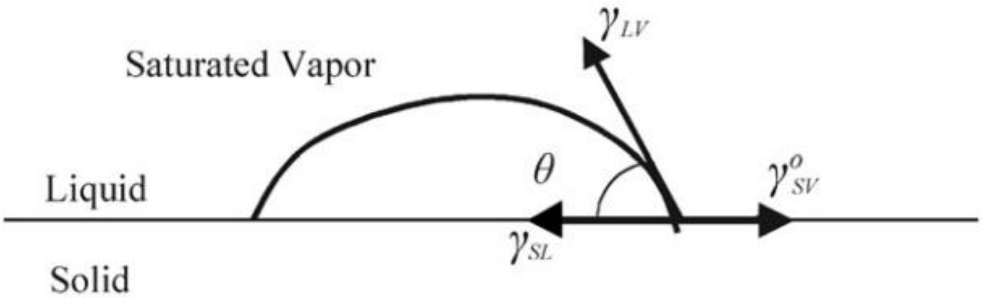

Figure 2.5: Solid-substrate Interfacial Tensions (Ebnesajjad, 2011)

2.6 Application of Photocatalytic

Technology has advanced at a breakneck rate in the last few decades. New technologies arise and supersede traditional approaches. The same goes for air treatment and self-cleaning, despite the fact that conventional air treatment is still extensively utilised across the world. A variety of technologies and methods have been developed to improve the efficiency and practicability of air treatment. For instance, photocatalytic technologies. Photocatalytic technologies are widely acknowledged as potential solutions to environmental concerns. Many applications have been discovered, varying from anti-microbial, self-cleaning surfaces, anti-fogging to photovoltaic hydrogen generation and water and air purification. Most of these have widespread use in real-world applications.

2.6.1 Application of Photocatalytic for Air Purification

The scientific community has spent more than three decades working to develop photocatalytic methods for removing a variety of air contaminants. Photocatalysis has been shown to be effective at removing pollutants from the gas phase at low concentrations. Various photocatalytic compounds have been suggested (Alalm et al., 2021). Heterogeneous photocatalysis using titanium dioxide (TiO_2) as a catalyst is a fast growing subject in environmental engineering, with enormous potential to address rising pollution levels. In 1996, Japan pioneered the use of TiO_2, in the photo-active crystalline phase anatase, as an air purification material. Since then, a wide range of methods for both indoor and outdoor uses have come on the market (Boonen and Beeldens, 2014). The application of photocatalytic coating for air purification can be categorised into three levels which are bench-scale, pilot and full. The majority of the research is done on a bench scale or pilot scale. However, just a few field experiments have been done in full scale under real-world settings; this is due to the conditions are different and uncontrollable. A user-friendly method for cementitious surfaces was created using aqueous suspensions of TiO_2 nanoparticle-based photocatalytic surface coatings and a remediation technique for NOx emission and organic pollution removal. NOx removal efficiencies were assessed using hydrophobic and hydrophilic photocatalytic TiO_2 sols for dip and spray coating on cement tiles. When applied to concrete surfaces, hydrophobic photoactive TiO_2 NP-based coatings shown an exceptional capacity to convert NO gas. For TiO_2 loadings over 5%, hydrophobic TiO_2 coated cement tiles showed a 90% decrease in NOx pollutants, suggesting that the coating might be advantageous for highly contaminated locations near pollution sources (Faraldos et al., 2016). In another research, a photocatalytic TiO_2 layer was coated over the pavement blocks. According to the research, the hydrophilic characteristics of the TiO_2 surface hampered NOx adsorption on the paving block surface due to competition between NOx and water vapour for access to the catalyst's active sites. A total of 200 g of TiO_2 were required to convert ambient NOx to NO_2 at a rate of approximately 0.0046 mg/m^2/min (Dewi, Khair and Irsyad, 2016). Using an ISO 22197-1 procedure for measuring NO in air purification, Luna et al. (2019) improved the preparation of Au-TiO_2/SiO_2 coatings and demonstrated their efficacy in photooxidizing NO. The enhanced photoactivity of Au NPs has been linked to the observed selectivity for NOx elimination and the potential activation of O_2 and NO molecules by strong adsorption, which might increase NO oxidation.

Based on a handful of the novel TiO_2-samples, PureTi Clean, Evonik and P25, Zhu, Koziel and Maurer (2017) created photocatalytic coatings for barn walls and ceilings for reducing interior smells. The researchers use simulated evaluations to learn about these paints' effects on reducing odorous VOC emissions, with stimulated circumstances containing a few organic substances such as diethyl sulphide, dimethyl disulfide, dimethyl trisulfide, butyric acid, p-cresol and guaiacol. With a photocatalyst loading of 10 μg/cm^2, the pure Ti-based coating removed most of the odour components. TiO_2 photocatalysis was being considered by certain Japanese firms, by mixing colloidal TiO_2 solutions with cement, NOx was eliminated from car exhausts utilising TiO_2-coated road bricks with sunlight. The photo-road technology was used at 14 different sites in Japan. Tokyo's 7th belt highway with a total surface area of 300 m^2 was used as a test site for the photo-road technology. NOx eliminated from this experiment area was around 50–60 mg/day, which is equivalent to the amount of NOx generated by 1000 vehicles (Serpone, 2018). A 2006 research in Bergamo, Italy, found a 30–40% drop in NOx content in a portion of a local roadway coated with photocatalytic paving stones for four weeks compared to an identical stretch left untreated (Peccati and Guerrini, 2007). In Segrate, Italy, a study found that a street concrete portion (7000 m^2) built with a thin coating of photocatalytic mortar reduced NOx emissions by 57%. In contrast, a study in Calusco, Italy, found that an 8000 m^2 pavement constructed with photocatalytic concrete blocks reduced NOx emissions by 45%. However, investigations in Petosino, Italy and Brussels, Belgium discovered that photocatalytic NOx reductions were significantly lower than measurement accuracy errors (1–2%) (Gallus et al., 2015b; 2015a). In Hengelo, the Netherlands, Ballari and Brouwers (2013) conducted a full-scale outdoor practical demonstration of air purifying pavement across the entire width of a roadway surface with a concrete pavement containing C-doped TiO_2 sprayed over a length of 150 m. For comparison, another 100 m section of the street was paved with standard paving stones; outdoor monitoring was carried out for 26 days. In order to determine the performance, each block was tested in a laboratory environment before and during the field tests. In May 2010, the initial coating was applied, showing positive outcomes in the lab and the area, with 7.7% NO and 6.9% NOx under visible light. Due to regular wear, vehicular traffic, weather, solid sand and filth accumulates upon the surface, the TiO_2 photocatalytic coating on the blocks was lost after 2.5 months of exposure to sunlight and weather. In September 2010, second coating was sprayed to the road. The photocatalytic performance was restored to the initial coating's levels after 1.5 months of street exposure. It was found that the average daily conversion of NOx to nitrates measured by chemiluminescence in the open air was 19.2 $\pm$ 17.8% and the afternoon conversion rate was 28.3 $\pm$ 20.0%, respectively.

2.6.2 Application of Photocatalytic for Self-cleaning

Since the concept of "self-cleaning" was first introduced based on the superhydrophobic property of lotus leaves, researchers from surface chemistry to material science have realised the importance of the self-cleaning principle in developing many innovative superhydrophobic materials for practical applications (Afroz et al., 2021). The photoactive self-cleaning materials can begin photocatalytic reactions capable of constantly cleaning their surface and treating air contaminants when exposed to natural solar light (outdoor) or LED irradiation (indoor). This method appears to be highly promising and it has piqued the industry's curiosity. As the first self-cleaning glass, Pilkington Glass' Activ^{TM} consists of a nanocrystalline TiO_2 layer placed on the glass surface of 15 nm thick. Furthermore, Activ^{TM}'s low visible reflectance (7%), favourable solar radiation absorption and transmittance characteristics make it ideal for self-cleaning applications (Banerjee, Dionysiou and Pillai, 2015). According to Guo et al. (2021) studies, TiO_2's enhanced self-cleaning capability may be accomplished by exposing the surface to a stream of water flow. Since the outside walls of buildings are expected to be exposed to ample sunshine and natural rainfall, self-cleaning may be effectively accomplished with TiO_2 coatings. A wide range of TiO_2-based self-cleaning building materials has been marketed, including cement, tiles, plastics, glass, aluminium slides and so on (Gopalan et al., 2020). The earliest experiments in the field of self-cleaning materials were conducted using enhanced TiO_2 in white cement mixtures. Initial findings were published in 1996 and the first large-scale building of this sort, the church Dives in Misericordia, Rome, was completed in 2003 and put into service in 2004 (Grebenişan et al., 2019). Photocatalytic cement-based material was intended to preserve its artistic features throughout the period, notably its colour even in harsh metropolitan contexts. It was stated by Folli and Macphee (2010) that a cement-based architectural element containing TiO_2 was able to preserve its aesthetic look over time and that this would help to keep surfaces exposed to certain contaminated environments cleaner. Figure 2.6 demonstrates that the anatase TiO_2 photocatalytic cement-based exterior chapel walls did not stand the passage of time. Besides, the National Opera Hall in China is protected by self-cleaning glass that has been coated with a layer of TiO_2 photocatalytic nanoparticles (Bai, 2005). Finally, self-cleaning tiles have been used to cover thousands of tall structures in Japan. Since 2003, the PanaHome Company, one of Japan's largest home manufacturers, has promoted "eco-life"-style houses that include self-cleaning windows and tiles and a solar panel–covered rooftop (Liu and Jiang, 2012).

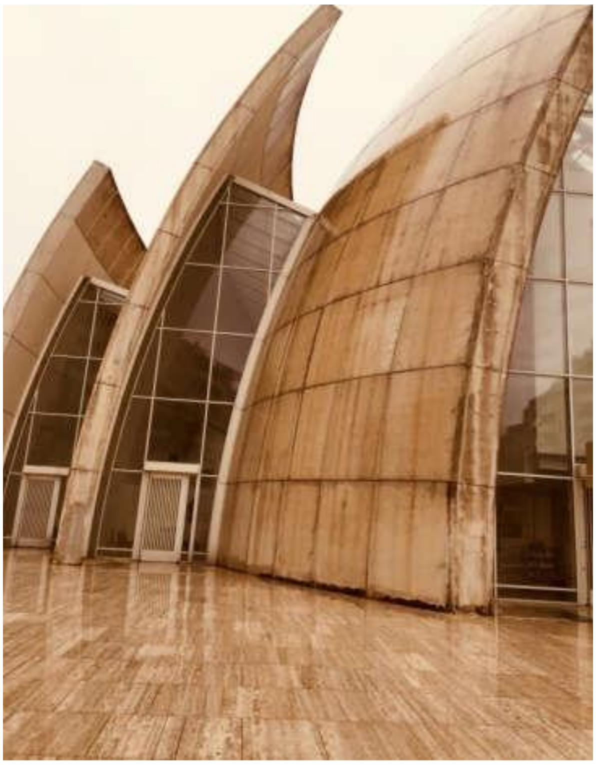

Figure 2.6: External Walls of Church After a Period of Time (Serpone, 2018)

For applications such as solar panels, solar thermal collectors and greenhouses, self-cleaning TiO_2 coatings with small surface reflection/anti-reflection properties and good light transmission are advantageous. In addition, for practical applications, the hydrophilic nature of self-cleaning coatings should also be maintained for a long time, even in the absence of light. However, in the absence of light irradiation, the photoinduced superhydrophilic nature of pure TiO_2 film progressively reverts (Banerjee, Dionysiou and Pillai, 2015). Because of the small particle sizes utilised, there will be more efficiency in filling gaps and preventing corrosive components from flowing through the nanocoating (Abdeen et al., 2019). In addition, the nanocoatings' high grain density gives improved adhesion qualities, which will enhance the coating's lifespan. As a result of their superior mechanical and electrical characteristics, nanocoatings are stronger, tougher and better resistant to wear and corrosion. To some extent, paint development has been affected by nanocoating technology (Schuh, Nieh and Iwasaki, 2003; Sriraman et al., 2013). The coating process of the surface and nanocoating deposition is a crucial stage that describes the structure of the surface and influences its corrosion characteristics.

By using the sol-gel technique, followed by hydrothermal post-treatment, anatase TiO_2 nanoparticles were deposited on the stainless steel surface, increasing its corrosion resistance when evaluated in Ringer solution. It was found that when tested in a NaCl solution, three or four layers (464 nm thickness) of TiO_2 nanoparticles on the surface of stainless steel specimens proved to offer the highest corrosion resistance when prepared using the same process. Compared to bare steel, this homogeneous coating reduced corrosion current density about three times and enhanced corrosion resistance approximately ten times (Shen, Chen and Lin, 2005; Shen et al., 2005).

When a photovoltaic (PV) module is positioned in a particular environment, its performance and power production are directly impacted by dust and airborne filth deposition on the module's front cover, mostly glass or a polymer. The dust buildup on solar cell glass panels is primarily determined by the tilt angle, orientation of PV panels and surface roughness (Said and Walwil, 2014). Li et al. (2018) examined the effect of dust buildup on solar cell glass panels. The results revealed that dust buildup might cause a 32% drop in solar panel performance, amplifying the plate-transmittance loss (Abushgair and Al - waked, 2021). Applying a coating to the cover glass of solar cells is one way to reduce temperature and dust without installing any additional hardware. Ultraviolet photons are absorbed by a special substance in the coating, which is then re-emitted in the visible band with decreased energy. This would reduce the amount of heat created by photons while also reducing dust buildup (Denholm et al., 2010). The self-cleaning effect of a superhydrophobic surface on a solar cell panel has been widely discussed, but there have been no findings demonstrating how effective it is (Nosonovsky and Bhushan, 2009). Bhushan, Yong and Koch (2009) exhibited self-cleaning effectiveness for several types of synthetic superhydrophobic surfaces by using this cleaning concept. Despite the fact that their study included a detailed assessment of the cleaning effectiveness of several surfaces, none of the surfaces they investigated was suitable for solar cell panels in practice. On the contrary, Zhu et al. (2010) used nanoscale morphology to demonstrate the self-cleaning function of nanodome solar cells. This research gave some understanding of the concept of self-cleaning solar panels generated *via* changing the structural morphology of the photovoltaic cells. However, it is challenging to put these findings into reality on a big scale and marketed solar panels. Furthermore, the lack of a comparison with the experimental data (cleaning impact on a standard photovoltaic cells surface) might prompt readers to consider the need for self-cleaning coatings on photovoltaic panels. As a result, the future uses of solar cells will require an apparent superhydrophobic surface with an easy production method and a better cleaning performance when compared to current normal surface solar cells.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Methodology Flowchart

A literature review examines books, academic papers and other resources related to a specific subject, field of research or theory. It provides a definition, overview and critical analysis of certain publications relevant to the research topic under consideration (Fink, 2014). This study is separated into five distinct phases. First, the research problem was formulated in order to determine the area of photocatalytic coating that was necessary. Following that, do a search and assessment of sources by reading articles and books. After reading those published journals, do an analysis of the material. The presentation of the review findings is choosen to convey the previously decided-upon topic. Finally, write a paper about photocatalytic coating. Figure 3.1 depicts the methodology flowchart to achieve the above mentioned key phases.

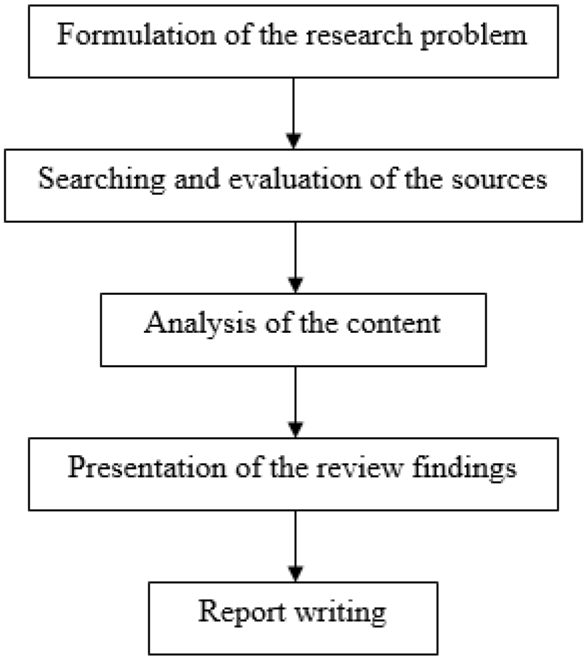

Figure 3.1: Flowchart of Methodology

3.2 Formulation of the Research Problem

A research question is a mean to convey curiosity about a topic or phenomenon. Each inquiry should be clear and concise, address the problem and indicate an experimental activity intervention. By defining a research question will help to concentrate study or determine the path of inquiry (Boudah, 2011). Furthermore, it assesses the study's effect and contribution to the target audience and research community. The research problem must be evaluated to see if any related literature reviews exist (Onwuegbuzie, 2016).

In this review, it was first identified the area of photocatalytic coating required for assessment. The topic of application of photocatalytic coating for air purification and self-cleaning was chosen because it represented one of the critical global concerns that the public is likely to be interested in. It was also confirmed that there were relatively few publications in the chosen area. Because of the rapid advancement of technology in this globalised age, the primary substance of this research was condensed and concentrated on the current development and future potentials of photocatalytic coating. The variations in photocatalysis should be summarized and reviewed to understand its impact on air purification and self-cleaning efficiency. The study findings and outcomes can help to realise the potential of photocatalytic coating in air treatment.

3.2.1 Searching and Evaluation of the Sources

The next step was to start looking through books and journals. Review techniques should comprise developing a search strategy, study selection, study quality evaluation, data extraction, data synthesis, managing papers and bibliographies (Torres-Carrion et al., 2018). To begin the search, it is usually a good idea to decide which online libraries and databases to use first (Pautasso, 2013). Table 3.1 lists the databases used for this research.

Table 3.1: Online Libraries and Databases

Online Libraries/ Databases	**Website Address**
UTAR Library	https://library.utar.edu.my/
ScienceDirect	https://www.sciencedirect.com/
Elesivier	https://www.elsevier.com/en-xs
Google Scholar	https://scholar.google.com/
ResearchGate	https://www.researchgate.net/
PudMed	https://pubmed.ncbi.nlm.nih.gov/

Despite the abundance of publications available from online sources, screening was advised to identify credible sources that would be retrieved for research (Lau and Kuziemsky, 2016). It is critical to analyse each source in order to establish the quality of the information included within it. The evaluation of sources follows some standard evaluation criteria, including the writers' credentials and reputations, publishing date, purpose, objective or bias (Mandalios, 2013).

Following that, the pertinent publications were retrieved and arranged using paper management software. Several management systems can be found online and widely used by researchers such as Mendeley, Papers, Qiqqa, Sente and etc. (Pautasso, 2013). Mendeley was the paper management software used in this instance. Mendeley is a reference management software that helps users quickly organise and categorise downloaded articles and create citations. Figure 3.2 depicts the software's main interface. Journals or publications that Mendeley did not recognise were excluded from the data collecting procedure.

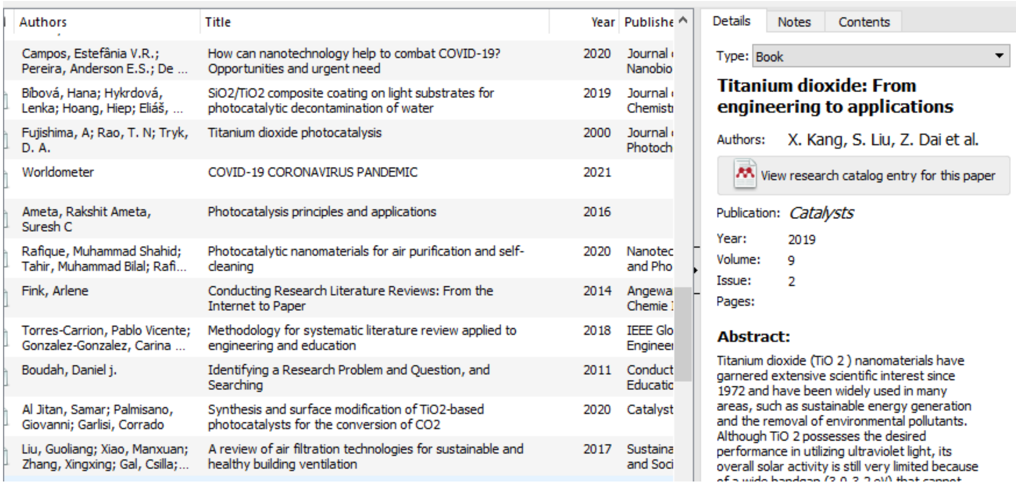

Figure 3.2: Main Interface of Mendeley

3.2.2 Analysis of the Content

Following that, a comprehensive reading of the selected journals was performed. An essential factor, in this case, was evaluating human errors. Human errors are always possible during the analysing process; these errors might be caused by weariness, incorrect interpretation and personal prejudice (Bengtsson, 2016). According to Kitchenham et al. (2009), publication bias is an issue in which good results are more likely to be publicised than negative consequences. Thus, it was the researcher's job to ensure the validity and reliability of the procedure throughout the whole investigation, as the outcomes must be as rigorous and trustworthy as feasible (Bengtsson, 2016). Jesson and Lacey (2006) stated that a good journal article should summarise the current theory, authors and works from the beginning. Data analysis and synthesis must involve the following steps: collect, summarise, aggregate, arrange and compare the evidence retrieved from the included research. The collected data must be presented in a meaningful manner that implies a novel addition to the existing literature (Lau and Kuziemsky, 2016).

Additionally, the documentation of publications was conducted in this phase. The papers were read and re-read to acquire a feel of the overall picture before being organised into folders (Machi and McEvoy, 2016). Grouping aids the writing process in the final literature review presentation. Depending on the nature and scope of the individual review, the sample might be choosen in various ways. One of the approaches is to do the review in phases. Abstracts were reviewed first before deciding whether to read the entire text. As reading every piece of literature might be time consuming. Once this step was completed, combine it with other relevant articles that have been gathered previously. The texts were thoroughly reviewed again to ensure that it fulfills the inclusion criteria (Snyder, 2019).

3.2.3 Presentation of the Review Findings

The literature review procedure ultimately reached its conclusion, which was the presenting of review results. There are several methods to convey the review. Argumentative, integrative, historical, methodogical, systematic and theoretical literature reviews were among the review approaches (Pautasso, 2013). Based on the many options accessible, a systematic literature review (SLR) was used to create a well-formulated research question on the use of photocatalytic coating for air purification and self-cleaning. This form provides an overview of existing evidence related to a clearly stated research topic. It employs pre-specified and standardised techniques to discover and critically appraise relevant research. The goal is to purposefully document, critically analyse and scientifically synthesise all studies on a clearly defined research issue (Kennedy, 2007; Fink, 2014; Booth, Sutton and Papaioannou, 2016). In shorts, the review's findings were provided both qualitatively and quantitatively. Furthermore, because the systematic review was based on extensive literature searches in a variety of search engines, the problem of subjective selection bias was eliminated (Pae, 2015). Systematic reviews were ideal for mapping, analyzing and synthesising literature to establish an understanding about photocatalytic coating applications for air purification and self-cleaning.

3.3 Report Writing

A report is a written presentation of factual data based on study or experiment. Reports are frequently used to solve issues or make choices in the fields of business and science. Its nature and purpose heavily influence the structure of each report. In general, a well-written report is clear, logical, unambiguous and straightforward while keeping the document's objective in mind (Bappah and Yarima, 2015). Reports are formatted in a consistent manner. This makes it easier for the reader to discover information and concentrate on specific topics.

According to Forsyth (2010), a report is separated into three sections which include the beginning, the middle and the end.

This report, title page, acknowledgments and table content were provided at the beginning of the report page. Follow that, an abstract or executive summary. The abstract gives a synopsis of the whole study. It describes the study's objective, methodology, findings, significant conclusions and suggestions. The introduction of photocatalytic coating comes next. In this context, a brief introduction to photocatalytic coating was provided, as well as the goal and scope of the report, which covers the key difficulties or problems and the rationale for completing the study. Moving on, the literature review, methodology and the result and discussion. These three sections can be categories as the middle. The literature review was conducted to investigate papers published by researchers by summarising and comparing the work of those publications. Methodology is known as a process of data collection or techniques of data analysis. It tells the reader what method was used to collect data for this study. Results and discussion give the finding of this study clearly and precisely. It had included the review findings, outcome discussion, analyze and state implications. Lastly is the conclusion. The conclusion summarises the key findings of the paper. It informs readers of the study's limitations and makes recommendations. The reference style used in this paper is Harvard (Anglia Ruskin University).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Application of Photocatalytic Coating for Air Purification

Photocatalytic coating has been studied for decades and is regarded as an appealing solution for the remediation of organic air pollutants such as volatile organic compounds (VOCs), odours and the disinfection of airborne microbes at room temperatures. In photocatalytic coating techniques, ultraviolet (UV) light is commonly utilised as the light source, although new generations of visible-light active TiO_2 also show significant promise (Hamal and Klabunde, 2007; Yao and Lun Yeung, 2011). There has been an exponential increase in the number of patents published in the previous ten years. Figure 4.1 depicts the cumulative number of published articles and patents per year since 2012, with a focus on articles and patents containing the keywords "air purification" and "photocatalytic coating" as keywords. Although these diagrams do not represent all published articles and patents in photocatalytic air treatment applications, the identified trend demonstrates the great interest of inventors in this topic.

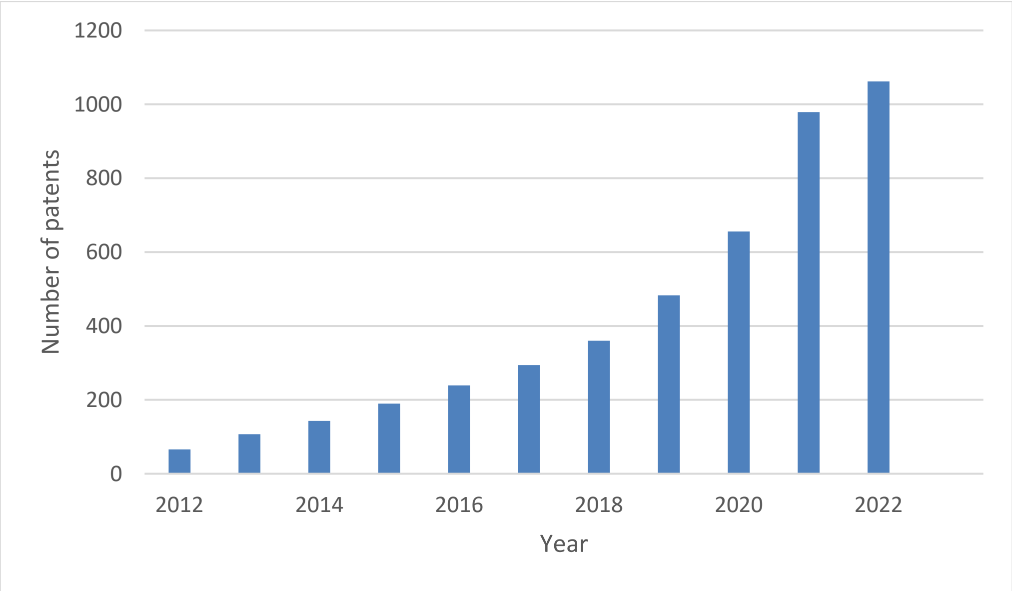

Figure 4.1: The total number of published patents for air purification photocatalytic coating (2012–2022) with the title's keywords " air purification".

4.1.1 TiO_2 and Modified TiO_2

Titanium dioxide (TiO_2) is a versatile photocatalyst with a wide range of uses. Titanium dioxide (TiO_2) is by far one of the superior semiconductors, owing to its excellent stability and photosensitivity, strong oxidation ability, minor toxicity and inexpensive cost. TiO_2 is a metal that occurs naturally in a variety of forms (Escobedo and Lasa, 2020). The three polymorphs of TiO_2 found in nature are rutile, anatase and brookite. Anatase and rutile type TiO_2 is a tetragonal crystalline system. However, anatase has lattice constants of $a_o = b_o = 3.78$ Å and $c_o = 9.50$ Å, while rutile lattice constants are $a_o = b_o = 4.58$ Å and $c_o = 2.98$ Å. Brookite, an orthorhombic crystalline form with $a_o = 9.17$ Å, $b_o = 5.43$ Å and $c_o = 5.13$ Å (Etacheri et al., 2015). Deformed TiO_6 octahedra are joined differently by corners and edges in all three crystalline forms. Anatase has the highest overall photocatalytic activity among these three forms (Molinari et al., 2017). Figure 4.2 shows the crystal structure of three forms of TiO_2, which includes rutile, brookite and anatase.

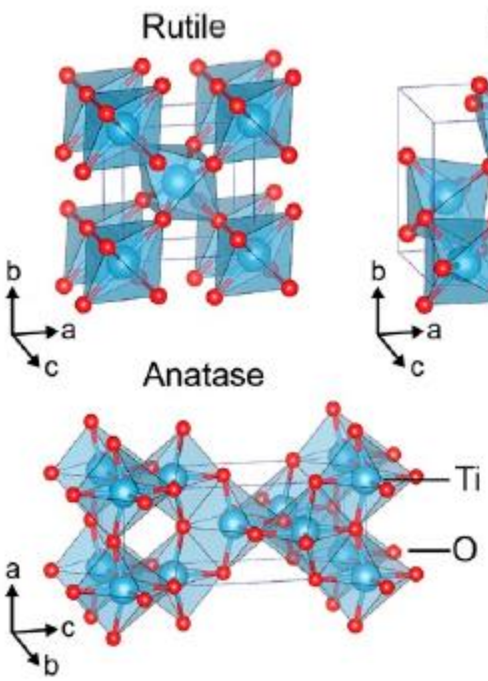

Figure 4.2: Anatase, Brookite and Rutile Crystal Structures (Haggerty et al., 2017)

In heterogeneous photocatalysis on the surface of TiO_2, there are five main steps, namely, photoexcitation (light absorption and charge carrier production), diffusion, trapping, recombination and oxidation (Gaya and Abdullah, 2008; Foo and Hameed, 2010). The effectiveness with which electrons and holes are channelled into oxidation and reduction processes before recombination determines the efficiency of photocatalytic reactions. Due to the recombination of holes and electrons, titanium dioxide's activity in photocatalytic processes is typically modest as it has a wide bandgap of 388 nm (3.2 eV), a disadvantage for photocatalysis usage (Zhu and Wang, 2017b). It is critical to improve the efficiency of titanium dioxide-based photocatalytic processes in order to apply this approach on a large scale (Mogal et al., 2013). One attempt has been made to improve its efficiency is by doping (Zhu and Wang, 2017a). Doping is the process of insertion of impurities (guest atom) into a substance (host substance) with the goal of altering its physical or electrical properties. Doping allows one to take advantage of empty sites and defects in the atomic structure of the host material. Modifying a material seldom entails a complete change in its underlying qualities but rather an improvement in its properties for diverse uses. Depending on the dopant type, whether metal or nonmetal, a dopant can raise the valence band (VB) edge level or drop the conduction band (CB) level, thereby minimising the bandgap (Gerischer and Heller, 1992; Ameta and Ameta, 2016).

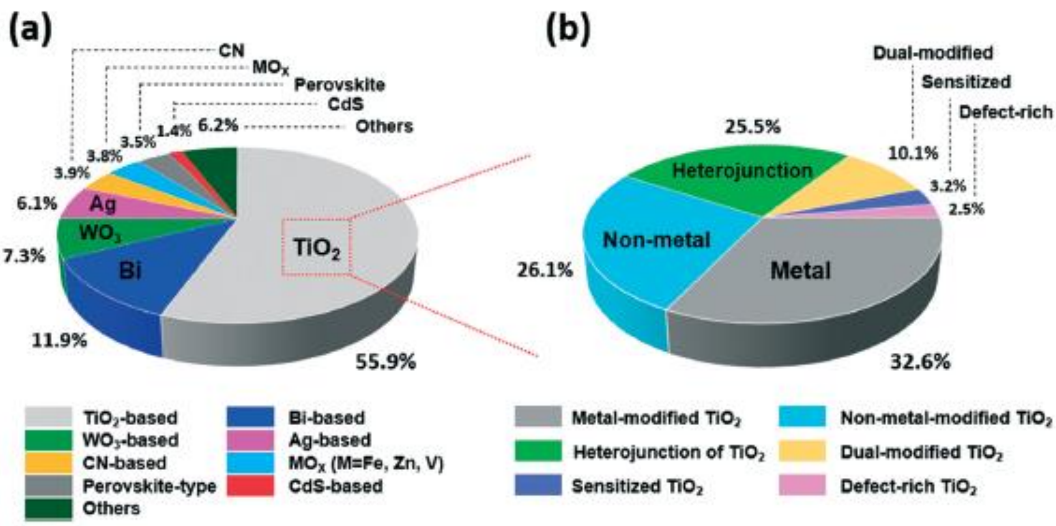

Figure 4.3: Breakdown of articles from 1999 to 2018 on visible-light photocatalysts and modified TiO_2 (Weon, He and Choi, 2019)

TiO_2 was the most investigated semiconductor among other semiconductors, as seen in Figure 4.3. It also demonstrates that metal doping of TiO_2 accounts for 32.6% of all investigations conducted by researchers from 1999 to 2018. Metal doping can be categorised into few subcategories which includes, transition metals doping (vanadium (V), iron (Fe), chromium (Cr), nickel (Ni), copper (Cu)), precious metals doping (gold (Au), ruthenium (Ru), platinum (Pt), silver (Ag), rhodium (Rh), palladium (Pd),) and rare earth metals doping (cerium (Ce), lanthanum (La), neodymium (Nd)). Metal oxides and noble metals have been reported to render TiO_2 visible light sensitive (Yu and Brouwers, 2009). Noble metals minimise electron-hole recombination, improve contaminant decomposition rates and limit photocatalyst deactivation (Wei et al., 2005; Vanderspurt et al., 2009). Manganese (II) oxide (MnO) decomposes ozone (O_3) in TiO_2/MnO composites (Wei et al., 2005). Additional metal oxides in Au-TiO_2 catalysts are being studied to reduce Au nanoparticle migration. WO_3/TiO_2 catalysts are also less susceptible to humidity changes (Wei et al., 2007). Nevertheless, metals are often costly and can disrupt the crystal structure in various ways. As a result, metals are rarely employed as carries (Li, Li and Zhou, 2020).

Aside from metal doping, TiO_2 may be modified in a variety of ways. For instance, non-metal doping, heterojunction, carbon-based material loading and alkali modification. All of the strategies mentioned above help to improve electron and hole separation and prolong light absorption into the visible region. Loading TiO_2 with carbon-based compounds and distributing TiO_2 on inert supports increases the concentration of surface electrons, improves surface adsorption of reactants, particularly CO_2 and reduces agglomeration of TiO_2 nanoparticles (Corma and Garcia, 2013). However, the light usage efficiency is reduced since they absorb and scatter a portion of the radiation, resulting in photon waste (Meryem et al., 2017). Although TiO_2-based heterostructures are complicated to synthesise and are regarded as unstable, they boost TiO_2 semiconductor photocatalytic efficacy and efficiently segregate oxidation and reduction sites (De_Richter, Ming and Caillol, 2013). Table 4.1 below outlines the benefits and drawbacks of the main modification methods.

Table 4.1: Benefit and Drawbacks of TiO_2 Modification Strategies (al Jitan, Palmisano and Garlisi, 2020)

Modification methods	Benefits	Drawbacks
Metal Doping	-Improves the separation of electrons and holes -Increase the visible spectrum of light absorption	-Costly -Disrupt the crystal structure
Non-metal Doping	-Improves the separation of electrons and holes -Increase the visible spectrum of light absorption	-Serve as recombination hubs
Heterojunction	-Effectively separate oxidation and reduction sites -Improves the separation of electrons and holes	-Complicated synthesis technique -Unstable
Carbon-based Material Loading	-Increases the concentration of electrons on the surface -Enhance the surface adsorption of reactants -Minimise the aggregation of TiO_2 nanoparticles	-Prevents TiO_2 from absorbing light
Alkali Modification	-Improves the separation of electrons and holes -Improves CO_2 chemisorption	-TiO_2 nanoparticles encapsulation

TiO_2-containing photocatalytic coating efficiently eliminates the ozone precursors NO and NO_2 when exposed to UV light with approximately 80% and 30%. The photocatalytic modification of NO was observed to rise as relative humidity decreased from 50% to 20%, while the photocatalytic rate was determined to be between 0.11 µg m^{-2} s and 0.42 µg m^{-2} s, depending on the humidity level (Maggos et al., 2007). To evaluate the removal over TiO_2 containing mineral silicate coating irradiated with UV light, VOCs including such benzene and toluene, which seem to be major airborne contaminants in indoor and outdoor environments, were investigated in an efficient building for real life, as individual components and as mixes (Fujishima, Zhang and Tryk, 2008). The results were positively favourable, indicating that TiO_2 coatings significantly degraded these chemicals as individual compounds or combinations. The experiment reveals that after 7 hours of irradiance, toluene was reduced to about 90% at a relative humidity of 20% and toluene degradation in a combination containing NO or benzene was quicker, reaching 90% after just four hours (Binas et al., 2016). According to Dewi, Khair and Irsyad (2016) study, TiO_2 coated on paving blocks can convert ambient NOx to nitrates due to photocatalytic efficiency. With an average temperature of 29.89°C, humidity of 45.31% and wind speed of 0.84 m/s, 200g of TiO_2 per 1 m^2 square paving block could transform ambient NOx to nitrate at a rate of 0.0046 mg/m^2/minutes. The average UV intensity was 71.82 µW/cm^2, with a NOx content of 0.066 ppm in the ambient air.

The application of photocatalytic coating to remove benzene, toluene, ethylbenzene and *o*-xylene (BTEX) and NO at average indoor air ppb values is possible. Under low humidity, 86% of BTEX and over 90% of NO were removed. For the photodegradation of BTEX, no deactivation was discovered. It was discovered that humidity has a significant impact on photodegradation. Both NO and BTEX conversions were greatly hampered by increased humidity. The promoting effect of NO was diminished when the residence period was reduced and it was also substantially reduced as the humidity increased (Ao et al., 2003). According to Pal et al. (2007), bacteria can be inactivated by TiO_2 in the presence of fluorescent light, which is routinely utilised as indoor illumination. Photocatalytic inactivation was most successful on *Escherichia coli* (abbreviated as *E. coli*). At the same time, it was least effective on *Bacillus* *subtilis* (abbreviated as *B. subtilis*), according to investigations on six strains of bacteria, four are Gram-positive and two are Gram-negative bacteria. Four bacteria demonstrated the greatest inactivation at optimal TiO_2 loadings ranging from 511 to 1666 mg/m^2. After 30 minutes of fluorescent irradiation at a TiO_2 dosage of 1666 mg/m^2, *E. coli* was completely inactivated. This TiO_2 loading can be applied on the interior walls routinely irradiated with fluorescent lights to cause indoor microorganisms to become inactive.

Platinum (Pt) and Palladium (Pd) are transition metals that have a greater ammonia affinity than gold (Au) and silver (Ag). On the TiO_2 surface, transition metals may be employed to oxidise ammonium molecules to dinitrogen selectively. Pt catalyses anoxic breakdown of alkylamine pollutants by interacting with the nitrogen atom's lone-pair electron. This method only works on electron lone-pair neutral alkylamines (Dongil, 2019). Localised surface plasmonic resonance (LSPR) is a characteristic of gold and silver nanoparticles that have been used for photocatalysis. When visible light strikes nanoparticles in the 20–100 nm range, the free electron charge oscillates, causing electron transfer from the photoexcited metal to the conduction band (CB) in TiO_2. This has been used in photocatalysis using visible light (Sellappan et al., 2013). Harikishore et al. (2014) generated nanocrystalline pure TiO_2 and five mol% silver-doped TiO_2 (Ag–TiO_2) powders using the sol-gel technique. The bandgap of TiO_2 was lowered from 3.1 to 2.9 eV after Ag was added. The degradation of methylene blue (MB) was used to test the photocatalytic activity. Within 24 hours, the development of *E. coli* was completely stopped. Compared to as-synthesised TiO_2, the best efficiency was recorded when TiO_2 was annealed at 500°C. However, the efficiency declined when the temperature was increased. The average particle size was estimated to be between 6 and 15 nm. The mesoporous TiO_2 catalyst is a stable and very effective solution for the visible light photodegradation of VOCs when modified with tiny amounts (0.5 wt%) of indium vanadate ($InVO_4$). The photocatalysts' long life is attributed to $InVO_4$'s stable sensitizer under visible light irradiation. The formation of superoxide radical anion ($O_2^{\bullet-}$ and $OH^{\bullet}$) explains the relatively high photocatalytic activity of $InVO_4/TiO_2$ under visible light irradiation, resulting in effective VOCs breakdown (Xiao et al., 2008). Wang et al. (2009) have studied, in the presence of l-cysteine, C–N–S-tridoped TiO_2 nanocrystals were produced using a simple biomolecule-controlled hydrothermal technique. L-cysteine, a biomolecule, might act as a standard supply of carbon, nitrogen and sulphur and regulate the final crystal phases and shape. Under simulated solar light irradiation, the C–N–S-tridoped TiO_2 nanocrystals had substantially better photocatalytic efficiency than the commercial P25 and the undoped photocatalyst on eliminating the prevalent indoor pollutant NO. The visible light absorbance and bandgap narrowing of TiO_2 nanocrystals due to C–N–S-tridoping were primarily responsible for the increased photocatalytic activity.

In summary, TiO_2 whether pure or modified, has been shown to be an effective material for decomposing organic and inorganic air contaminants (Lorencik, Yu and Brouwers, 2016).

4.1.2 ZnO, WO_3 and other Photocatalyst

Many researchers were interested in zinc oxide (ZnO) particles because of their UV absorption uses (Mädler et al., 2002). Its mineral name is zincite and it may be found in nature. The mineral is generally yellow to red in colour and contains a small quantity of manganese and other metals. ZnO is an n-type semiconductor with a large bandgap of 3.37 eV that belongs to the II-VI semiconductor group. Because of its broad bandgap, ZnO has the potential as a photocatalyst material (Klingshirn, 2007). Besides, ZnO has gotten a lot of attention because of its high photosensitivity, which causes various contaminants to degrade (Gancheva et al., 2016). ZnO also has a significant exciton binding energy of 60 MeV (Shakti and Gupta, 2010). The two primary types of zinc oxide crystallise are hexagonal wurtzite and cubic zinc blende, with the wurtzite structure being the more frequent (Ameta and Ameta, 2016).

Due to its unique chemical functional and physical features, tungsten trioxide (WO_3) has piqued scientific attention. WO_3 is a transition metal oxide with a moderate indirect bandgap between 2.4 eV and 2.8 eV, and it outperforms TiO_2 and ZnO for photocatalytic applications (Baeck et al., 2003). It is an excellent photocatalyst for visible and UV light applications. WO_3 nanoparticles have a high surface-to-volume ratio, as well as energy and quantum confinement features (Zheng et al., 2011). However, due to the fast recombination of photo-induced electron-hole pairs, WO_3 is still a long way from being a practical semiconductor for photocatalysis applications. Because electron transfer to the oxide's conduction band is a surface phenomenon, it is expected that the bigger the semiconductor's specific surface area, the more photo-induced electron-hole pairs may be moved to the oxide's surface to activate photocatalysis activities (Tahir et al., 2017). As a result, doping WO_3 with other metals improves its performance by shifting its conduction band towards the negative (Zhang et al., 2013).

Lavand and Malghe (2015) used a microemulsion approach and successfully manufactured pure and nitrogen-doped ZnO nanospheres. The nanosized N-doped ZnO was found to be spherical and to have a wurtzite phase. Nitrogen insertion into the oxygen site of ZnO induces lattice compression. Compared to commercial and pure ZnO nanoparticles, N doping significantly increased the light absorption efficiency of ZnO in the visible range and demonstrated better photocatalytic activity. The nanosized N-doped ZnO as-prepared was found to be very stable and reusable. Gondal et al. (2009) used a UV laser-generated photocatalysis technique in the presence of iron (III) oxide (Fe_2O_3) semiconductor catalysts to efficiently remove phenol. Variations in laser irradiation period, laser intensity and catalyst concentration were used to examine the influence of operational factors on the removal process. During the 1-hour irradiation, the maximum phenol elimination more than 90% was attained. With the help of carbon-sphere templates, Liu et al. (2015) created flower-type vanadium pentoxide (V_2O_5) hollow microspheres with sizes of 700–800 nm. These were employed in the visible light photodegradation of 1,2 dichlorobenzene (o-DCB). Due to its excellent adsorption capacity and wide specific surface area, the V_2O_5 hollow structure demonstrated high photocatalytic activity in the destruction of gaseous o-DCB under visible light. The presence of intermediates such as o-benzoquinone-type and organic acid species and ultimate degradation products CO_2 and H_2O was also verified. Jašková, Hochmannová and Vytřasová (2013) investigated the antimicrobial properties of ZnO NPs. The coating with the lowest concentration of nano-ZnO (1 vol. %) was efficient against bacteria *E. coli* and *Staphylococcus aureus* (abbreviated as *S.aureus*). Increased nano-ZnO concentration in coatings increased *Pseudomonas aeruginosa* (abbreviated as *P.aeruginosa*) and *Aspergillus niger* (abbreviated as *Tiegh*) suppression. Even the greatest concentration of ZnO (4 vol.%) tested was insufficient to suppress the fungus

Penicilliumchrysogenum. Table 4.2 summarises photocatalyst composition with air purification application.

The methods described in the recent patents, which are comprehensively reviewed clearly indicate the need to create various materials capable of improving the effectiveness of photocatalytic air purification while also achieving a cost-effective procedure. In the last ten years, doping TiO_2 with other semiconductors or metals has been suggested as a possible remedy. Nevertheless, TiO_2 remains the most common material in various applications, including air purification, where it is doped or combined with other oxides or active compounds.

Table 4.2: Photocatalyst Composition and Air Purification Application

Photocatalyst	Application	Reference
TiO_2	Eliminates NO and NO_2, up to 80% and 30%.	Maggos et al., 2007
TiO_2 containing mineral silicate	Remove VOCs such as toluene and benzene.	Fujishima, Zhang and Tryk, 2008
TiO_2	Able to convert ambient NOx to nitrates and remove benzene, toluene, ethylbenzene and *o*-xylene (BTEX) over 86% and 90%.	Dewi, Khair and Irsyad, 2016
TiO_2	Inactivated microorganisms such as *E. coli*.	Pal et al., 2007
TiO_2 surface with transition metals	To oxidise ammonium molecules to dinitrogen selectively. Pt catalyses anoxic breakdown of alkylamine pollutants.	Dongil, 2019
Ag–TiO_2	Reduced TiO_2 bandgap from 3.1 to 2.9 eV. Within 24 hours, the development of *E. coli* was completely stopped.	Harikishore et al., 2014
$InVO_4$/TiO_2	Effectively breakdown VOCs.	Xiao et al., 2008
C–N–S-tridoped TiO_2	Eliminating the prevalent indoor pollutant NO. Bandgap narrowing of TiO_2 nanocrystals due to C–N–S-tridoping.	Wang et al., 2009
N-ZnO	Improved the light absorption efficiency of ZnO in the visible range and demonstrated better photocatalytic activity	Lavand and Malghe, 2015
Flower-type V_2O_5	Photodegradation of 1,2 dichlorobenzene (o-DCB).	Liu et al., 2015

4.2 Application of Photocatalytic Coating for Self-cleaning

The use of self-cleaning building materials is one of the intensively researched methods of eliminating various airborne contaminants (Daoud, 2013). In urban or industrial areas, building materials made of such components would considerably impact in terms of increasing aesthetics and enhancing air quality. According to research studies, interfaces made of self-cleaning building materials with a contact angle of <10° can be classified as hydrophilic/super hydrophilic, aiding the removal of water pollutants, for example, during rainfall (Chermahini et al., 2018). Furthermore, oleophobic-hydrophilic materials having a contact angle of <10° for water and >150° for non-polar substances can lower the quantity of adsorbed dirt and simplify impurity removal. Last but not least, photocatalytic additives can degrade pollutants (Yang et al., 2012). Apart from skyscrapers or building materials, photocatalytic coating could be used in textiles for antimicrobial and self-cleaning purposes, such as removing dye, stain on fabrics, etc. The statistical analysis of the current research trend is shown in Figure 4.4. Which photocatalytic material is most commonly studied for self-cleaning in 2012-2022, with the keywords "self-cleaning" and "photocatalytic coating".

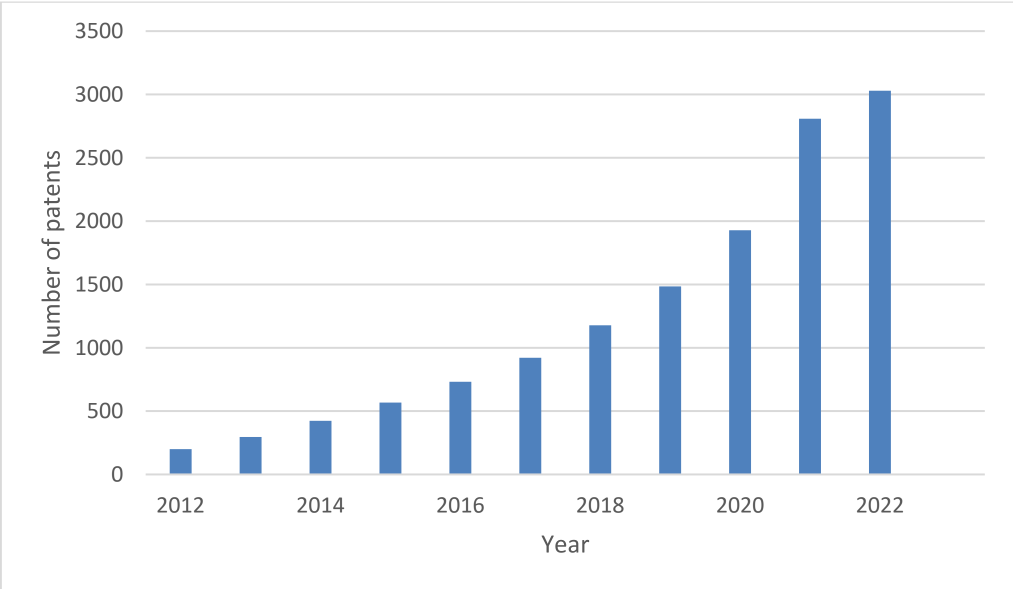

Figure 4.4: The total number of published patents for self-cleaning photocatalytic coating (2012–2022) with the title's keywords "self-cleaning".

4.2.1 TiO_2 and Modified TiO_2

TiO_2 has been employed as a disinfection component in implications of photocatalytic coating for sound absorption covers installed along underpass wall surfaces, operating room wall surfaces, slab roadways, streets and highways (Shakeri et al., 2018). Photocatalytic layers, which allow for odour elimination are formed upon porcelain construction materials, for instance, washroom tiles (Future Markets, 2014). The inclusion of TiO_2 provides for the reduction of a variety of chemical molecules, including aliphatic alcohols, halogenated compounds, alkanes and amines. Organic molecules decompose into less harmful chemicals such as CO_2 and H_2O in the photodegradation process (Banerjee, Dionysiou and Pillai, 2015). The contact angle of water clinging towards the exterior under the impact of radiation is also affected by TiO_2 surface chemistry. When TiO_2-coated surfaces are exposed to radiation, they become ultrahydrophilic, but the surface slowly regenerates and becomes hydrophobic when the radiation is turned off. The coating's ultrahydrophilic characteristics are restored after re-irradiation (Ludwig, 2010). The shift of the structure from hydrophilicity to hydrophobicity is influenced by the adsorption of organic molecules on the TiO_2 film surface. The photocatalytic breakdown of these organic pollutants will cause the TiO_2 coating to self-clean and the surface to preserve its superhydrophilicity (Hamidi and Aslani, 2019).

A self-cleaning coating for window panes was the first product based on solar photocatalysis using TiO_2 (Zhao et al., 2008). Using a chemical vapour deposition approach, a layer of nanocrystalline anatase TiO_2 was formed on soda-lime silicate float glass. This glass has a high level of optical transmission and reflection (Mills et al., 2003). Because of the high hydrophilicity of TiO_2 layer, inorganic and organic particles adsorbed on TiO_2-coated surfaces are quickly degraded and subsequently washed away with water, as in self-cleaning tiles. TiO_2 is one such material that considerably slows down and in some cases entirely stops the growth of *Algae Chlorella vulgaris* on building facades. TiO_2 as a building material modification also improves the purifying effectiveness of algae such as *Chlorella mirabilis* and *Chroococcidiopsis fissurarum* when flush pollutants *via* rainwater. After an hour of intense irradiation, *Escherichia coli* cells on the TiO_2 covering are killed. Mild UV visible light and copper or silver alteration of TiO_2 has also been reported to improve antibacterial characteristics

(Hashimoto, Irie and Fujishima, 2005). By putting a photocatalytic membrane over a ceramic matrix, Liu P., X.-C. Wang and X.-Z. Fu (2000) created self-cleaning ceramic materials. They looked at how photocatalytic activity of these materials affected oleic acid decomposition and sterilisation. The influence of preparation and reaction circumstances such as heating treatment and membrane thickness was also detected on the photocatalytic activity of the self-cleaning ceramics. They concluded that the supported photocatalyst membrane's specific surface area, particle size and crystal structure affect oleic acid photodegradation and sterilisation of self-cleaning ceramics.

Luna et al. (2019) changed TiO_2 *via* doping it with nitrogen (N) and adding gold (Au) nanoparticles to increase its photoactivity under the presence of solar light. Furthermore, Au/N-TiO_2 photocatalysts were added to the silica sol to spray it onto three distinct construction material substrates, which are limestone, granite and concrete. The findings revealed that gold nanoparticles (Au-NP) boosted the photocatalytic activity of TiO_2 nanoparticles, tripling the quantity of NOx eliminated in UV light irradiation. Compared to the coatings applied to limestone, the coatings were more effective in eliminating pollutants from concrete. Zaleska (2008) modified TiO_2 containing carbon and nitrogen (C and N), which came from methanol, ethanol, isopropanol and ammonia (NH_3) gas, respectively. The TiO_2-N, C changed in this manner was added in varied proportions by weight to bricks, cement pavers and gypsum ranging from 1% to 20% by weight. The test findings revealed that photocatalysts were the most efficient in terms of photocatalysis for materials comprising 10% by weight of TiO_2-N-C.

Tents made of polyvinyl chloride (PVC) are notoriously difficult to clean. Chemical resistance and self-cleaning characteristics were improved when photocatalytic polytetrafluoroethylene (PTFE) and PVC membranes containing TiO_2 were utilised. Not only that, but such constructions keep their beautiful looks and light transmission for a longer time. Storage structures, bus stops, railway stations, playgrounds, park and beach canopies might benefit from self-cleaning tent materials (Kallio et al., 2006; Yuranova, Laub and Kiwi, 2007). Deng et al. (2014) employed a sol-gel technique to manufacture titanium dioxide-silicon dioxide@polydimethylsiloxane coatings (TiO_2–SiO_2@PDMS) with exceptional superhydrophobic and photocatalytic properties. When calcined at 470°C, these films displayed superhydrophilicity and had good thermal stability up to 400°C. On a broad scale, the TiO_2–SiO_2@PDMS hybrid solution was utilised to coat polyester-cotton textiles, making them superhydrophobic. These textiles have superhydrophobicity, which is resistance to assault by powerful acids. This fabric might be used as a filter cloth for oil-water separation as well as printing vivid patterns. Meilert, Laub and Kiwi (2005) used non-toxic spacers to cover commercial Degussa P25 TiO_2 on cotton fabric to create self-cleaning fabric. Succinic acids, 1,2,3-propanetricarboxylic and 1,2,3,4 butanetetracarboxylic acids were used as spacers to activate cotton fabric containing functional groups on the surface. Then, Degussa P25 TiO_2 was applied to the fabric's surface using the dip-coating procedure. This titanium spacer cotton degraded a range of stains, including intense coffee, make-up solution, red wine and simulated human sweat with increased photocatalytic activity. Daoud and Xin (2004) created self-cleaning cotton using a traditional pad-cure-dry procedure to add TiO_2 nanosol to cotton fabric. A sol-gel technique was used to nucleate TiO_2 from titanium tetra isopropoxide. Under UV irradiation, the TiO_2 coated cotton cloth was found to break down organic pollutants and grime. Different synthetic textile pre-treatment procedures have been investigated to see if TiO_2 coatings may fade coffee and wine stains under visible light in an acceptable amount of time. Temperatures of 100°C or lower were revealed to be adequate for attaching TiO_2 to synthetic fabrics after post-treatment. After photochemical stain discolouration, TiO_2 nanoparticles remain relatively durable on the textile surface. Using a simulated solar light with 50% AM1, a combination of titanium tetra isopropoxide colloids and TiO_2 powder applied on wool-polyamide or polyester fabrics was revealed to be kinetically appropriate for the self-cleaning of coffee and wine stains (Bozzi, Yuranova and Kiwi, 2005).

4.2.2 ZnO, WO_3 and Other Photocatalyst

ZnO also has a number of advantages, including a reasonable price, a large number of active sites with high surface reactivity, excellent light absorption efficacy and environmental safety (Kong et al., 2009). Shan et al. (2015) used a sol-gel/ spin-coating process to coat copper-bismuth (III) oxide (Cu–Bi_2O_3) films with SiO_2. The photocatalytic efficiency and self-cleaning activity of the as-prepared films were investigated using stearic acid decomposition. In comparison to pure Bi_2O_3 films, these films demonstrated exceptional superhydrophilic capabilities even in the dark, as well as enhanced photocatalytic and self-cleaning properties. It was concluded that the interfacial charge transfer between Bi_2O_3, Cu and SiO_2 improved the rate of photocatalytic degradation and self-cleaning. These films were also effective as antifogging materials. The wettability and photocatalytic investigations of SnO_2, ZnO, and ZnO/SnO_2 thin films produced on glass substrate using the sol-gel spin coating process are reported by Talinungsang et al. (2019). The results demonstrate that ZnO/SnO_2 thin films have a superhydrophilic property as well as a high degree of transparency. Model contaminants in the solid and liquid phases were used to investigate the films' photocatalytic activity. Compared to ZnO and tin (IV) oxide (SnO_2) thin films, ZnO/SnO_2 thin films were shown to be more efficient. The charge recombination was suppressed due to the creation of a heterostructure between ZnO and SnO_2. They believe that a superhydrophilic film with excellent transparency might be beneficial in antifogging and self-cleaning applications. Moafi, Shojaie and Zanjanchi (2011) created self-cleaning cellulosic fibres by grafting ZnO nanoparticles on the fibre's surface using a simple sol-gel procedure at room temperature. The thermogravimetric measurements revealed that ZnO makes up roughly 18% of the weight of the modified fibre and is tightly attached to the support surface. When pre-adsorbed MB and eosin yellowish (EY) are exposed to ultraviolet-visible (UV–vis) light, ZnO-modified cellulosic fibres with tiny particle size distribution have strong photocatalytic self-cleaning characteristics. The photodegradation process was aided by ZnO nanoparticles supported on cellulosic fibre and the large surface area associated with the tiny particle size offers a suitable environment for self-cleaning. The nano-ZnO coated fibres demonstrated outstanding reusability and self-cleaning capabilities, which are critical for the formation of intelligent textiles that are stain resistant.

The sol-gel powder dispersion thin film phases were used to make composite tungsten oxide/ reduced graphene oxide (WO_3-rGO) thin films. The composite powders were made using two methods which are adding rGO commercial powder to crystalline WO_3 powder inside the dispersion stage (Route 1) and adding rGO instantly to the oxide precursor approach to make combined WO_3–rGO sol, gel and powder (Route 2). During photocatalysis, the thin films produced using Route 1 were demonstrated to possess superhydrophilic water contact angles (CA) smaller than 10°, visible active and very stable. These films achieved photodegradation efficiencies of around 25% with modest UV-Vis irradiation of 34 W/m^2, with roughly 5% ascribed to adsorption. This demonstrates that the films become visible activated when rGO was added to the WO_3 layer and were suitable for self-cleaning applications (Covei et al., 2019). Liu et al. (2021) developed a self-cleaning photocatalytic WO_3-TiO_2 nanorod (MWT) fluorine-free building coating with good durability and NO degradation performance. The building application's durability and self-cleaning capabilities were assured based on this article. At the same time, the long-term efficacy of photocatalytic coatings has significantly been enhanced thanks to the addition of self-cleaning capabilities. The self-cleaning photocatalytic MWT building coating provides the groundwork for future research into environmentally friendly and energy-efficient materials. Self-doped tin (IV) oxide/graphene oxide (SnO_2-x/GO) composite photocatalysts with high visible photocatalytic activity were successfully produced and utilised to manufacture cotton textiles with very efficient and lasting self-cleaning activity. The outcomes showed that the existence of oxygen vacancies increased light absorption significantly and GO effectively promoted the separation of photogenerated electron-hole pairs, both of which were influenced by the molar ratio of Sn^{4+}/Sn used to make SnO_2-x and the amount of GO in SnO_2-x/GO. When the $Sn^{4+/}$Sn molar ratio and the GO concentration was 4:1 and 5%, respectively, the best photocatalytic activity of SnO_2-x/GO was reached with the methyl orange solution (MO) photodegradation rate constant of 0.13233 min^{-1} and 0.15290 min^{-1}. In the presence of SnO_2-x/GO completed cotton textiles, the MB photodegradation ratio reached up to 99%. The hypothesised process and reactions for SO_2-x/GO constructed cotton fibres may significantly impact the creation of self-cleaning textiles (Qi et al., 2019). Table 4.3 summaries the self-cleaning application with photocatalyst composition.

Table 4.3: Photocatalyst Composition and Self-cleaning Application

Photocatalyst	Application	Reference
Anatase TiO_2	Coated on soda-lime silicate float glass, inorganic and organic particles adsorbed on TiO_2-coated surfaces are quickly degraded and subsequently washed away with water.	Zhao et al., 2008
TiO_2	Improves the purifying effectiveness of algae such as *Chlorella mirabilis* and *Chroococcidiopsis fissurarum* while flushing pollutants through rainfall.	Hashimoto, Irie and Fujishima, 2005
TiO_2	TiO_2 over a ceramic matrix, created self-cleaning ceramic materials. Removal of oleic acid decomposition and sterilisation.	Liu P., X.-C. Wang and X.-Z. Fu, 2000
Au/N-TiO_2	Spray onto limestone, granite and concrete. Tripling the quantity of NOx eliminated in UV visible light.	Luna et al., 2019
TiO_2–SiO_2@PDMS	Coated on polyester-cotton textiles making them superhydrophobic. This fabric might be used as a filter cloth for oil-water separation and vivid patterns.	Deng et al., 2014
Titanium dioxide Degussa P25	Coated on cotton fabric to create self-cleaning fabric. Degraded red wine, intense coffee and make-up solution.	Meilert, Laub and Kiwi, 2005
ZnO	Nano-ZnO coated fibres demonstrated self-cleaning capabilities, formation of intelligent textiles that are stain resistant.	Moafi, Shojaie and Zanjanchi, 2011
SnO_2-x/GO	SnO_2-x/GO completed cotton textiles, MB photodegradation ratio reached up to 99%. Significantly impact the creation of self-cleaning textiles.	Qi et al., 2019

4.3 Future Perspective of Photocatalytic Coating for Air Purification and Self-cleaning

Both developed and developing countries are facing a lot of emerging issues regarding the air and environment. Globalisation has resulted in significant air pollution resulting from economic growth. To make it worse, humans could encounter problems of coronary heart disease, cardiovascular disease, lung diseases and respiratory infections (Jiang, Mei and Feng, 2016). Industrial waste gas and car exhaust gas are the primary sources of air pollution today. Hence, integrating the latest air treatment technologies is essential for maintaining a healthy air environment.

Researchers have been paying more attention to photocatalysts to break down air pollutants since the invention of photocatalysis (Zhou et al., 2021). Toxic gases in the atmosphere could be adsorbed or decomposed by photocatalytic material, decreasing the negative impact of poisonous gases on the environment. Semiconductor photocatalysis is mild and the reaction is straightforward. Photocatalysis has the potential to destroy nearly all contaminants in the air. As a result, unlike traditional technologies such as adsorption, ozone oxidation, plasma and filtration, photocatalytic technology may totally destroy pollutants in the air under sunlight, allowing for quick air purification (Zhang et al., 2019). Photocatalysis is a technique with a wide range of applications and a lot of room for advancement.

On the other hand, the recent SARS-CoV-2 (COVID-19) viral outbreak opens up new possibilities for photocatalytic coating. Today, hospitals could be a potential application for photocatalytic coating. The photocatalytic coating could aid in the creation of safely enclosed areas with proper patient separation and medical worker protection (Gharaibeh, Smith and Conway, 2021). The photocatalytic coating could help prevent COVID-19 breakouts in other hospital areas by keeping enclosed hospital spaces uncontaminated (Prakash, Cho and Mishra, 2022). Another situation is dental clinics, where it is now mandatory to keep enclosed spaces free of contamination. As a result, new technologies for "on-site" photo-inactivation of the COVID-19 virus are required (Kumaravel et al., 2021).

Present photocatalysts demand UV light irradiation to induce the accelerated oxidation action. As a result, the photocatalytic activity's efficiency is significantly reliant on the UV intensity of incident light (Yan et al., 2013). However, overexposure to health-damaging UV radiation is a big worry. Furthermore, UV light accounts for only 0.1% of indoor lighting, thus limiting the photocatalytic air purification and self-cleaning effect's efficacy in indoor applications (Kumar et al., 2016). As a result, in order to improve photocatalyst usability, the photocatalyst's efficacious absorption wavelength range must be expanded to encompass different areas, including visible light or infrared light (Tung and Daoud, 2011). Visible-light activation of TiO_2 can be achieved using one of the modifications mentioned above or bandgap engineering techniques (Etacheri et al., 2015).

In recent years, photocatalytic air purification and self-cleaning materials have seen rapid technological advancement. However, there has been no accepted international specification for verifying the efficiency and safety of these materials until now. Given the promise of such materials and their wide range of applications, a set of universal empirical testing standards for objectively describing and evaluating the performance of newly discovered air purification and self-cleaning materials is urgently needed. Government control and labelling prerequisites for the manufacture and usage of nanocrystalline TiO_2 functionalized self-cleaning fibrous materials are likewise required in terms of safety (Tung and Daoud, 2011).

Another future research priority will be designing and fabricating smart self-cleaning surfaces with self-healing capabilities. For scientists and engineers, discovering from ecology has served as a source of bioinspiration (Liu and Jiang, 2011). For instance, Wong et al. (2011) recently developed slippery liquid–infused porous surfaces and self-healing by increased optical transparency, inspired by *Nepenthes* pitcher plants. These innovative permeable surfaces surpass their natural counterparts by repelling a wide range of liquids such as blood, crude oil, hydrocarbons, insects as well as water. The multipurpose smart surfaces developed will be beneficial in the medical field, optical sensing, transportation and self-cleaning in harsh environments. Different solutions have evolved in nature to accomplish efficient multifunctional integration. As a result, more interdisciplinary collaboration is required to build multifunctional smart self-cleaning surfaces for science and engineering researchers (Liu and Jiang, 2012).

4.4 Challenges of Photocatalytic Coating in the Future Development of Air Purification and Self-cleaning

Despite the fact that photocatalytic coatings have been shown to be superior and brilliant at removing impurities from the air, most of the research has been done in batch and lab-scale tests. However, in order to be truly implemented in real-world air treatment, a small amount of photocatalytic coating will not be enough to meet the growing air pollution.

The limited use of ambient light, principally visible light and infrared is one of the key limitations of photocatalytic coating that prevents its practical implementation in air purification (Etacheri et al., 2015). The most researched topic and desired goal in environmental photocatalysis have been visible light use. Still, it should be noted that visible light can be used at the expense of redox power (Weon, He and Choi, 2019). Because visible light excitation produces fewer energy electrons and holes than UV excitation, visible light cannot degrade stubborn air contaminants that require strong oxidants (He, Jeon and Choi, 2021). Therefore, visible light photocatalysis might not be the ideal choice for air purification applications. It should only be used when ambient visible light like room light or sunshine is utilised as a light source (Xu et al., 2020). In general, modified TiO_2 materials are not that effective in visible light absorption. Despite this, their high oxidation power, which is mostly governed by the strong positive charge of the TiO_2 valence band edge, outstanding stability across a wide range of circumstances, low material price and nontoxicity, cause TiO_2 barely replaceable as viable environmental photocatalysts (Singh and Dutta, 2018).

Due to the photodegradation of internal paint components in the presence of photogenerated reactive oxygen species (ROS), the increased activity of photocatalytic coatings has a detrimental impact on coating service life (Petronella et al., 2017). As a result, it is difficult to create a long-lasting and effective photocatalytic coating for long-term self-cleaning applications.

Recent scientific investigations have found some techniques for extending the service life of photocatalytic coatings. Non-photooxidizable binder systems, an intermediate protective layer, a film thickness of smaller than 1 μm and photocatalytic concentration optimization are all potential strategies for generating lasting photocatalytic self-cleaning coatings (Fernando et al., 2022). However, none of these solutions has been thoroughly and systematically examined in recent studies aimed at prolonging the life span of photocatalytic coatings. To improve photocatalytic activity and service life, an organised evaluation of the influence of binder type, film thickness, protective layer and photocatalyst concentration will become an essential study topic (Petronella et al., 2017).

The key to achieving superhydrophobic behaviour is to reduce the surface energy of a coated material. This can be accomplished by coating the fabric surface with perfluorinated compounds with long carbon chains between 8 and 12 carbon atoms (Schellenberger et al., 2019). However, it has been shown that these elements can accumulate in live creatures and create health issues such as cancer, immunological disorders and hormonal disruption (Ju et al., 2017). Furthermore, these compounds can be released into the environment through the fluoropolymer production process, product washing, wear off during usage and heat degradation (Zahid et al., 2019).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Summing up the entire review, researchers worked hard to improve air purification and self-cleaning using photocatalytic coatings. Photocatalytic coating was denoted as a potential nanomaterial to replace the conventional filtration method such as high efficient particulate air (HEPA) filters, electrostatic (ES) filters and activated carbon (AC) filters in removing bacteria and NOx from air pollution. In comparison to HEPA, ES and AC filters, photocatalytic coating can totally breakdown pollutants. Furthermore, because photocatalytic coatings undergo a chemical reaction in the presence of light, they can save a significant amount of money on cleaning costs. Other advantages of this technology include environmental protection and do not produce secondary contamination (environmentally friendly). A short literature analysis was undertaken to investigate the impact of various semiconductors on photocatalytic coating applications and future perspectives for air purification and self-cleaning. From the review findings, TiO_2 was found to be a highly superior photocatalytic coating material. Meanwhile, it was also discovered that doping could lead to better performance of photocatalytic coating.

A feasibility study was conducted to fully comprehend the advantages of photocatalytic coating over alternative air treatment approaches. Using photocatalytic coating technology, the removal effectiveness of air pollutants such as *Escherichia coli* (*E. coli*), ozone and volatile organic compounds (VOCs) was greater than 90%. The superiority of photocatalytic coating has attracted a lot of attention in the future air purification and self-cleaning sector. In the coming years, increased research into photocatalytic coating as localised air treatment and self-cleaning technology is expected.

5.2 Recommendations for Future Work

There are various suggestions that can be implemented to improve the current results and provide better insight for future research by other scholars. The recommendations are listed below.

- In the research and development of photocatalytic coating, some present studies intended to create a hybrid air treatment system, with photocatalytic coating as the leading core. Membrane filtration, adsorption, ionic and electrostatic removal methods were combined in the integration of diverse treatment systems. As a result, it will be capable of removing a wide range of air contaminants. The best is yet to come for the hybrid process, as different combinations of air treatment technologies produce varied results that have yet to be explored.
- More topics warranted further investigation and research. Given that dangerous levels of air pollution are becoming more widespread in metropolitan areas as a troubling issue for humanity, the need to scale up bench-scale photocatalytic coating to industrial-scale swiftly became apparent. The improvements to photocatalytic coatings would be nought if the technology could not be scaled up to meet environmental requirements. As a result, industrial modelling methodologies should be investigated in order to make it easier to incorporate pilot-scale findings into mass reactor designs.
- The feasibility of photocatalytic coating can be further improved by modifying the nanoparticles' structure. The previously mentioned papers have already served as guidelines and directions for future study. Prioritize research into ways to improve the efficiency of these photocatalysts when exposed to visible light. Because indoors receive less UV radiation, the applications for indoors are limited. Although several ways of reducing the bandgap have been documented, success remains difficult, implying that new approaches are required.
- The current study has not thoroughly investigated the photooxidation mechanism and by-products created by various contaminants. As a result, future studies will need to focus on the photooxidation process and

kinetics of different types of contaminants in order to fully comprehend the entire self-cleaning reaction's environmental impact.

- Exploration on the methods of enlengthening the photocatalytic coating life was highly recommended as it directly involved the costing of photocatalytic coating. Photocatalytic coating has to be popularized in all corners of the world as every person deserves to have accessibility to safe and clean air.

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